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The Far Ultraviolet Absorption Spectra and Ionization Potentials of the Alkyl Halides. Part I

W. C. PRICE,* *The Physical Chemistry Laboratory, Cambridge, England*

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The absorption spectra of methyl iodide, bromide and chloride have been examined in the region 2000–1000A. The analysis shows that the bands are due to the excitation of non-bonding electrons localized on the halogen atoms. They can be fitted into Rydberg series which go to the two components of the doublet state of the molecular ion as limits. The values of the ionization potentials so determined are 9.49 and 10.11 volts for methyl iodide, 10.49 and 10.80 volts for methyl bromide, and 11.17 and 11.25 volts for methyl chloride. The separation of the two ionization potentials is in excellent agreement with those predicted by R. S. Mulliken, though their actual values are somewhat lower. The electronic and vibrational nature of the bands is discussed and some correlation of the spectra of the three molecules is made.

THE usefulness of far ultraviolet absorption data in the theory of the electronic structure of polyatomic molecules consists in giving the term values of some of the electrons in the molecule. It is also frequently possible to obtain some evidence as to the nature of these electrons, i.e., whether they are of a bonding or a non-bonding type. At the same time as the experimental work to be described here, was carried out, Professor R. S. Mulliken put forward a theory of the electronic structure of the alkyl halides with which the experimental results are in very good agreement.[1] He showed that the lowest states of the ions of these molecules are doublets which are formed by the removal of non-bonding $np\pi$ electrons localized on the halogen atoms. The doublet separation is predicted to be 0.625 volt for the iodides, 0.32 volt for the bromides and 0.08 volt for the chlorides. These values agree extremely well with the separations found in the present work. However the actual values of the experimentally determined ionization potentials are somewhat lower than the predicted ones. A tentative explanation of this as being due to dipole or charge displacement effects is given in Part II.

A description of the apparatus and technique employed by the author in obtaining these spectra has appeared in earlier papers.[2] The instrument was a vacuum spectrograph of the grazing incidence type fitted with a glass grating which gave a dispersion of about 2.3A/mm in the region 1800–1000A. The Lyman continuum was the background against which the bands were photographed, hydrogen being used as a conducting gas in the discharge tube. Specially pure samples of the alkyl halides were used. Small amounts of the vapor (20 cc at 1 cm pressure) were admitted at frequent intervals into the main body of the spectrograph and a constant rate of pumping was maintained. The extremely large volume of the spectrograph (about 200 liters) served to smooth out the pressure so that

* Senior 1851 Exhibitioner, Trinity College.

[1] R. S. Mulliken, Phys. Rev. **47**, 413 (1935).

[2] Collins and Price, Rev. Sci. Inst. **5**, 423 (1934).

it remained sensibly constant during an exposure of an hour's duration.

The far ultraviolet absorption spectrum of methyl iodide, part of which is shown in Fig. 1 (see also Fig. 1, Part II) starts at 2010A. The bands are discrete down to 1650A, where strong predissociation sets in. The effect of the predissociation diminishes as we go to shorter wavelengths and at 1400A, the bands become sharp again. They also become weaker and crowd closer together with decrease in wave-length after the manner of bands going to an ionization potential. The extinction coefficients of the bands in the region 2000–1600A, as given by Scheibe, Povenz and Lindstrom,[3] are of the order of 10,000 and a pressure of only a few thousandths of a millimeter is all that is necessary to bring the bands out strongly. Such extinction coefficients are enormously greater than those found in visible or near ultraviolet absorption bands and approach the values calculated theoretically for the photoelectric ionization continua of atoms. The bands in the region 2000–1600A, were first found by Herzberg and Scheibe[4] and have been investigated more recently by Henrici and Grieneisen.[5] As these authors worked with quartz or fluorite instruments and used the H_2 continuum they were unable to examine the nature of the absorption in the region below 1600A. Now the ionization potentials of the methyl halides, as determined by T. N. Jewitt[6] using a molecular ray method all lie between 9 and 12 electron volts, i.e., between 1350 and 1000A. It was therefore of interest to investigate whether discrete absorption bands merging into ionization continua could be found in this region. The spectra obtained in these experiments showed that this expectation was actually realized.

Fig. 1b shows the absorption spectrum of methyl iodide in the region 1400–1215A. It can be clearly seen from the picture that the bands form themselves into two groups. One of these converges to a limit in the neighborhood of 1300A and the other comes to a head around 1220A. Now there are two possible explanations for such a convergence of bands. The first is that the bands represent a vibrational progression leading to dissociation (e.g., the Schumann-Runge bands in oxygen); the second, that they are the bands of an electronic (i.e., Rydberg) series approaching an ionization potential. The chief argument against the first is that the bands appear at much too low a pressure to be associated with such a process. The arguments in favor of the second are: (1) electron impact experiments have shown that ionization of CH_3I occurs in this region (2) the higher members of the series conform fairly well to Rydberg formulas (3) the pressures at which the bands appear are those at which photo-ionization processes would be expected to be complete (4) finally this interpretation is in agreement with the theoretical expectations. The values of the ionization potentials obtained by the extrapolation of the higher members of the two groups in Rydberg formulas are 9.490 ± 0.002 and 10.115 ± 0.00 volts. The difference between the two ionization potentials (i.e., 0.625 volt) agrees extremely well with that predicted theoretically by Mulliken. It is also apparent that no vibration bands accompany the higher electronic transitions and hence his assignment of the bands to the excitation of a non-bonding electron also receives considerable support.

It can also be seen from Fig. 1b that all the bands are of a multiple character, the separations decreasing to zero with increase in electronic quantum number. These separations must be of an electronic rather than a vibrational nature. This is so on account of the fact that for very high electronic states the bonding power of the electron is practically zero. Vibration frequencies then tend to assume a constant value and do not decrease to zero in the manner of the observed separations. The fusing together of many molecular electronic series, as the limit is approached, is rather detrimental to the accuracy with which the higher members of a particular series can be measured. However this did not prevent it being possible to show that they conform very well to Rydberg formulas. From these formulas the ionization potentials could be obtained with an accuracy at least fifty times as great as that of electron impact de-

[3] G. Scheibe, F. Povenz and C. F. Lindstrom, Zeits. f. physik. Chemie **B20**, 283 (1933).
[4] G. Herzberg and G. Scheibe, Zeits. f. physik. Chemie **B7**, 390 (1930).
[5] A. Henrici and H. Grieneisen, Zeits. f. physik. Chemie **B30**, 1 (1935).
[6] T. N. Jewitt, Phys. Rev. **46**, 616 (1934).

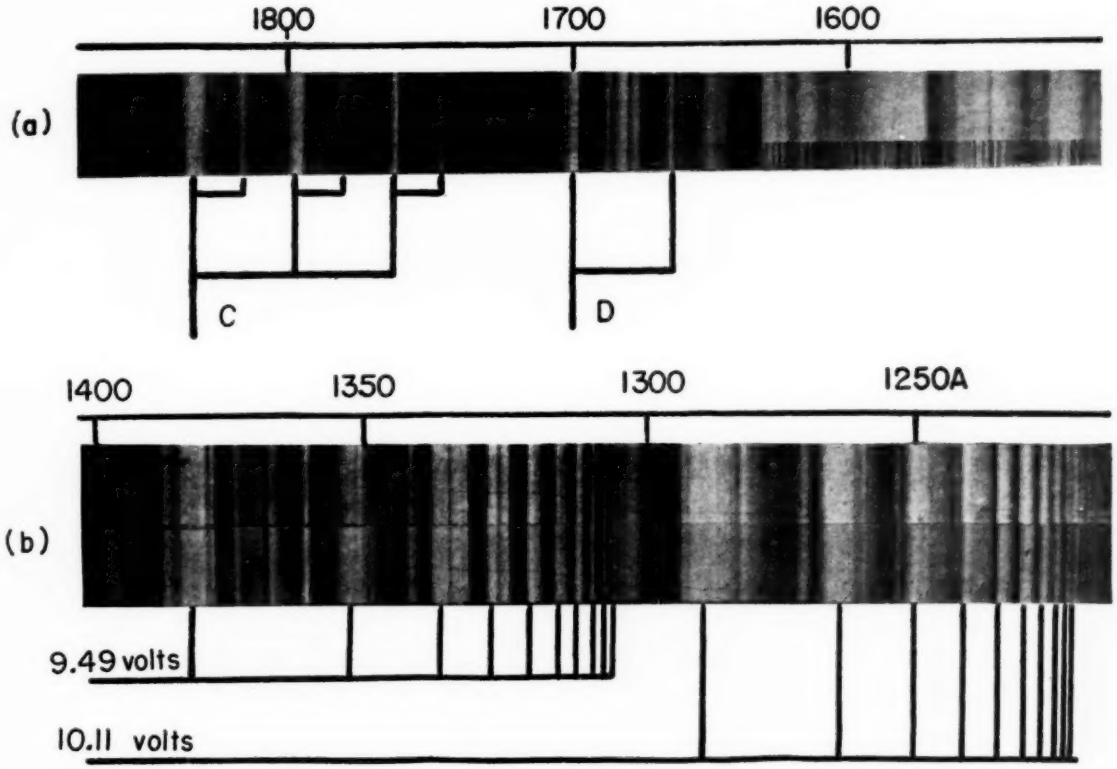

FIG. 1. The absorption spectrum of methyl iodide in the region (a) 1850–1550A, (b) 1400–1220A.

terminations. As it was only necessary to extrapolate in a Rydberg formula over 0.05 volt, the error in the extrapolation is extremely small. The strongest members of the respective groups were found to conform to the following Rydberg formulas with an accuracy that can be judged from Table I.

$$\nu_0^n = 76{,}930 - R/(n+0.75)^2, \qquad n = \cdots 6, 7, 8 \cdots, \quad (1a)$$

TABLE I. *Table showing the observed and calculated frequencies of the CH_3I bands of series (1a) and (2a).**

n	Series (1a) ν obs.	Series (1a) ν calc.	Series (2a) ν obs.	Series (2a) ν calc.	Observed Separation
6	74590	74521	79570	79617	4980
7	75125	75103	80160	80187	5035
8	75510	75500	80540	80573	5030
9	75780	75776	80855	80847	5075
10	75990	75980	81050	81049	5060
11	76145	76135	81205	81202	5060
12	76260	76255	81320	81320	5060
13	76345	76350	81425	81414	5080
∞	—	76930	—	81990	(5060)

* The series members $n = 1 \cdots 5$ are too strongly predissociated to be measured accurately. They also deviate from the simple Rydberg formula.

$$\nu_0^n = 81{,}990 - R/(n+0.80)^2, \qquad n = \cdots 6, 7, 8 \cdots. \quad (2a)$$

The other members could be fitted into analogous Rydberg formulas having the same limits as (1a) and (2a). These limits correspond to ionization potentials of 9.490 and 10.115 electron volts. The probable error in their determination is considered to be less than 0.003 volt (i.e., 20 or 30 cm^{-1}). Only the bands from $n=7$ to $n=14$ are represented really well by Rydberg formulas. It is difficult to identify many of the lower members in the region 1400–1600A because they are very broad and diffuse due to predissociation and they show considerable deviations from the simple Rydberg expressions. These deviations are probably due to two main causes. In the first place the iodine atom has a shell of 53 electrons and consequently even the atomic series with which the molecular series are associated would show considerable deviations from Rydberg types. Secondly a charge distribution or dipole effect due to the methyl

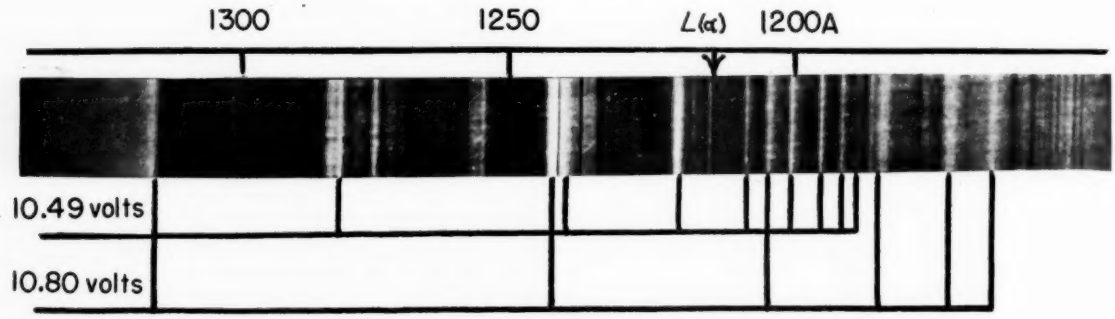

FIG. 2. The absorption of methyl bromide in the region 1300–1150A.

group must also influence the field in which the electron is escaping.

The $n=2.8$ terms of both (1a) and (2a) lie below 1600A while the $n=1.8$ terms seem to fall in the region of the long wave-length continuum (2200–2850A). It was originally thought that the B and C levels of Herzberg and Scheibe could be fitted in as first members of series (1a) and (2a). However, extremely large deviations from the simple formula would be required for this. More mature considerations and new data on the higher halides indicate that the B and C bands are different in type. They appear under the same conditions of pressure, etc., as the bands at shorter wave-lengths and also exhibit the constant electronic separation of $\sim$0.6 volt. It will be convenient to discuss them at a later stage when we deal with the higher halides.

It has already been mentioned that other electronic series besides those given by (1a) and (2a) were found to approach the two ionization potentials. In fact close to the limits it is apparent that each of the members given by these formulas has two accompanying bands, one on the long and one on the short wave-length side of it. Near the limits the positions of these bands can be obtained approximately by changing the Rydberg denominator in (1a) to $(n+0.50)^2 \cdots$ (1b) and $(n+1.0)^2 \cdots$ (1c) respectively for the lower limit. For the accompanying bands going to the upper limit the Rydberg denominator of (2a) has to be changed to $(n+0.55)^2 \cdots$ (2b) and $(n+0.95)^2 \cdots$ (2c). The series (1b) is particularly interesting because its bands which are double headed ($\Delta\nu\sim40$ cm^{-1}) can be followed right down to the first member of the series ($n=2$) which turns out to be the D band of Herzberg and Scheibe. The series (1c) and (2c) may possibly have the B and C bands as their first members but this could not be definitely established on account of the overlapping and the diffuseness of the intermediate series members.

The electronic separation of $\sim$0.6 volt can be traced right through the spectrum of CH_3I, from the bands between 2000 and 1600A right up to the separation of the two ionization potentials. It is, of course, not quite constant but varies from 4900 cm^{-1} (0.60 volt) for the Herzberg and Scheibe bands to 5060 cm^{-1} (0.623 volt) for bands close to the limits. On account of the similarity of the spectra of the different methyl halides it will be convenient to postpone a more complete discussion of the electronic nature of the spectrum, until the analogous spectra of methyl bromide and methyl chloride have been described.

THE SPECTRUM OF METHYL BROMIDE

The spectrum of methyl bromide is in many respects very similar to that of the iodide, and it has been interpreted in the same way by R. S. Mulliken. It has discrete bands which start around 1786A. Their extinction coefficients as given by Scheibe, Povenz and Lindstrom are somewhat less than those of the iodide, a result which is consistent with the fact that the excitation is from the halogen part of the molecule. In the present work the bands have been followed into the neighborhood of their ionization potentials, and, as is shown in Fig. 2, two limits have been found. On account of the fact that in the bromide these two limits are closer together than they are in the iodide, the overlapping of the upper members prevents them from appearing so distinctly. However, well developed Rydberg

series going to each ionization potential can easily be seen on a closer investigation of the bands. Consecutive members resemble each other in appearance and decrease regularly in intensity as we go towards shorter wave-lengths. There are not so many electronic series present in the bands of methyl bromide as there are in the iodide. In fact, most of the intensity is confined to two main electronic series, one of which goes to the lower and one to the higher limit. The Rydberg formulas which approximately fit the upper members of these series are the following;

$$\nu_0^n = 85{,}020 - R/(n+0.90)^2, \quad n=3, 4, 5 \cdots, \quad (3a)$$

$$\nu_0^n = 87{,}560 - R/(n+0.90)^2, \quad n=3, 4, 5 \cdots. \quad (4a)$$

The agreement of the values of the frequencies calculated from these formulas with those observed is given in Table II. The two limits correspond to ionization potentials of 10.488 and 10.803 volts respectively. The probable error is considered to be about 0.003 volt. The interpretation of the limits as ionization limits is supported by Jewitt's impact value of 10.2 ± 0.25 for the ionization potential of CH_3Br. The difference in the two ionization potentials ($10.803 - 10.488 = 0.315$ volt) is in very good agreement with that predicted by Mulliken though here again their absolute values are somewhat lower than those predicted. The causes of this have been discussed by Mulliken.[7]

The bands expressed by Eqs. (3a) and (4a) can be followed down to the $n=2$ members though they show increasing deviations for the values $n=2$ and 3. By putting $n=1$ in the formulas we predict bands which lie in the region of the B and C bands of Herzberg and Scheibe.

TABLE II. *Table showing the observed and calculated frequencies of the CH_3Br bands of series (3a) and (4a).*

	Series (3a)		Series (4a)		Observed
n	ν obs.	ν calc.	ν obs.	ν calc.	Separation
3	77980	77805	80360	80345	2380
4	80420	80450	82990	82990	2570
5	81880	81868	84400	84408	2520
6	82710	82715	85240	85255	2530
7	83260	83262	85820	85802	2560
8	83630	83635	86190	86175	2560
9	83895	83900	86450	86434	2555
10	84090	84096	—	—	—
∞	—	(85020)	—	(87560)	(2540)

[7] R. S. Mulliken, J. Chem. Phys. **3**, 514 (1935).

However the behavior of the latter bands with increase in the alkyl group is such that they cannot be identified with the series we are considering. They are in fact analogous to the B and C systems of CH_3I.

In addition to the series (3a) and (4a) two other weaker series were found in the bands. These are given approximately by changing the Rydberg denominator in (3a) to $(n+0.42)^2 \cdots$ (3b) and in (4) to $(n+0.45)^2 \cdots$ (4b). The first members of these two series are two strong sharp bands occurring at 66,020 and 68,680 cm^{-1}. They are apparently doublets ($\Delta\nu = 40$ cm^{-1}) and have a faintly discernible minimum down the center. The series (3b) and (4b) of CH_3Br are analogous in every way to the series (1b) and (2b) of the iodide. The band at 66,020 corresponds to the band designated by Herzberg and Scheibe as D in CH_3I.

As in methyl iodide the difference ΔV (0.315 volt or 2540 cm^{-1} for CH_3Br) is found to occur with only slight variation right throughout the spectrum. This is because of the fact that the variable terms in the corresponding Rydberg formulas are roughly the same.

The Spectrum of Methyl Chloride

In the same way that the first strong absorption bands of methyl bromide appear to the short wave-length side of the corresponding bands of the iodide, so the first bands of the chloride are shifted to the violet relative to those of the bromide. For reasons to be given later these bands, which appear around 1600A, are probably to be correlated with the B and C systems of the iodide. They are too diffuse for accurate measurements to be made on them. Considerably stronger bands occur at shorter wave-lengths and it will be shown that these are to be correlated with the D bands of methyl iodide. They start around 1400A, where there occurs a strong doublet $\Delta\nu = 650$ cm^{-1} accompanied by weaker bands on the short wave-length side extending out to 1320A. From 1320 to 1230A the spectrum is free from strong absorption bands. Just below 1320A there occurs another pair of absorption bands very similar to those around 1400A and having the same wave number separation. Other doublets were found at shorter wave-lengths.

However it was difficult to identify many of them with certainty because near the limits the bands become rather numerous and overlap. Also the weakening of the background due to continuous absorption from the C−H bonds increases the difficulties of observation (see Fig. 2a, Part II). It will be shown in Part II that whereas this absorption is negligible for the iodide and the bromide it becomes relatively stronger in the chloride.

The last weak discrete band of methyl chloride is observed at 1102A, i.e., 11.2 volts. The observed doublets approaching this wave-length were found to be represented approximately by the following Rydberg formulas,

$$\nu_0^n = 90{,}500 - R/(n+0.50)^2, \quad n = 2, 3, 4 \cdots, \quad (5)$$

$$\nu_0^n = 91{,}180 - R/(n+0.50)^2, \quad n = 2, 3, 4 \cdots. \quad (6)$$

The limits correspond to ionization potentials of 11.17 and 11.25 volts. On account of the proximity of the two ionization potentials there is considerable overlapping at the head of the series. Consequently there is a little uncertainty as to the assignment of some of the higher members. However in spite of this uncertainty the values of the ionization potentials are believed to be correct to 0.01 volt. The existence of ionization in this neighborhood has been shown by impact experiments. Jewitt's value for the ionization potential of methyl chloride is 10.7 ± 0.3 volts.

Table III gives the frequencies of the bands assigned to series (5) and (6) and also shows the persistent doublet separation of 650 cm^{-1}. This doublet separation agrees very well with the value that Mulliken has calculated theoretically for the lowest state of CH_3Cl^+ ($np\pi$ electron removed). Many other bands besides those of the two main series were present in the spectrum. They are relatively weak and most probably are vibrational bands accompanying the main electronic transitions.

TABLE III. *Table showing the observed and calculated frequencies of the CH_3Cl bands of series (5) and (6).*

	Series (5)		Series (6)		Observed
n	ν obs.	ν calc.	ν obs.	ν calc.	Separation
2	71110	(72940)	71760	(73620)	650
3	81480	(81542)	82150	(82220)	670
4	85110	85081	85790	85761	680
5	86870	86872	87570	87552	700
6	87900	87900	88550	88583	650
7	88550	88549	obsc.	89229	—
8	88970	88981	89650	89661	680
9	89300	89284	89960	89964	660
10	—	89505	90197	90185	—
∞	—	90500	—	91180	(680)

The calculated values of the frequencies of the first two members are bracketed, because as is to be expected they deviate considerably from the observed values.

The Electronic Nature of the Methyl Halide Bands

The following table shows the term values of the levels designated as A, B and D by Herzberg and Scheibe, referred to the lower of the two ionization potentials as limit. The D levels of the bromide are observed and classified for the first time in this work. For the A level the frequency of the maximum of the long wave-length continuum has been taken.

Band	CH_3I	CH_3Br	CH_3Cl
A	38300	33600	32600
B	27220	29000	28000
D	18060	19020	19390

It can be seen that the term values of the states which have been designated by the same letter do not differ very greatly as we go from iodide to chloride. This supports our correlation of them since it is expected that the term values of corresponding electronic states of atoms in the same column of the periodic table should be approximately the same within rather broad limits. A similar phenomenon would also be expected to occur in molecules where the excited states correspond to atomic orbitals. An example of this occurs in the absorption spectra of H_2O and H_2S[8] where corresponding electronic series have term values which do not differ very greatly.

Mulliken's assignment of the upper levels of the near ultraviolet continua (i.e., the A levels) of the methyl halides to an "s" orbital of the halogen atom implies that the continuous absorption is due to some strong form of predissociation rather than to transitions to a repulsive curve.* It has already been remarked that for the methyl iodide bands given by the formulas (1a)

[8] W. C. Price, J. Chem. Phys. **4**, 147 (1936).

* It will be shown in a subsequent article that the dissociation continua which arise from the excitation of non-bonding electrons can be explained by the collision of the electron in its excited orbit with bonding electrons in different parts of the molecule.

and (2a) the first members are predicted to lie in the long wave-length continuum. The fact that their second members, which occur around 1600A, are also strongly predissociated and that the predissociation diminishes as we go to shorter wave-lengths, supports the idea that the continua are to be linked up as the first members of the Rydberg series. A similar explanation has been found satisfactory for the continua of H_2O and H_2S. It is therefore probable that the upper states of the series (1a) and (2a) correspond to '*ns*' iodine orbitals. On account of the spherical distribution of the orbitals, the lower members penetrate considerably into the methyl group and the diffuseness is probably due to dissociation in this part of the molecule (i.e., the initial stage of the photodissociation). The higher members become sharper because a smaller and smaller fraction of the excited orbital is then finding itself in the neighborhood of the other atoms. It will be shown when the higher halides are considered, that the behavior of the bands with increase in the alkyl group (i.e., their shift to longer wave-lengths) also indicates that the excited orbitals penetrate considerably into this part of the molecule and thus supports their assignment to '*ns*' orbitals.

The *B* and *C* bands of methyl iodide are, according to Mulliken,[9] most probably to be ascribed to '$d\pi$' orbitals localized *near* the iodine atom. They suffer little wave-length shift and retain their sharpness for considerable changes in the alkyl group. This is to be connected with the fact that the orbitals are of an anchor ring distribution perpendicular to the C−I axis and thus do not penetrate the region of the alkyl group appreciably. Apparently with the possible exception of the iodide, higher members which form Rydberg series going to the ionization potentials, are not observed for this type of band.

A peculiar variation in the relative strength of the series is observed in going from the iodide to the chloride. In the iodide all three types (i.e., beginning on the *A*, *B* and *D* levels) appear fairly strongly. In the bromide only those beginning on the *A* and *D* levels could be established definitely. In the chloride the only strong series apparently starts on a level which is of a *D* type.

[9] R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935).

Vibrational Structure

The longer wave-length bands of the absorption spectrum of methyl iodide lie in the region where they can be studied with quartz or fluorite spectrographs using the H_2 continuum as a background. Their vibrational structure has been analyzed very satisfactorily by the investigators already mentioned in this article. It only remains for us to extend their well founded conclusions to the bands of the bromide and the chloride which lie at shorter wave-lengths, and to examine them in the light of the fact that the spectrum is due to the excitation of a non-bonding electron, which in the unexcited state is localized on the halogen atom. The original vibrational analysis was made possible by the discovery of selection rules limiting the types of vibration which can appear in the electronic spectrum of a polyatomic molecule. These rules are based upon an extension of the Franck-Condon principle to polyatomic molecules, and were first given by Herzberg and Teller [10] in an article in which they applied them to the ultraviolet absorption spectra of H_2CO, Cl_2O, SO_2, CH_3I etc. Earlier discrepancies have been cleared up and more examples of molecular spectra in which the rules are followed have been pointed out by Duncan.[11] For the simple case of absorption from a vibrationless ground state, the rules require that only the totally symmetrical vibrations are strongly excited in the upper electronic state.

Previous workers have found that in both the *B* and *C* states of methyl iodide there exists a vibrational progression of three or four members which diminish in intensity towards shorter wave-lengths. The bands are very narrow and have the approximate frequency separation of 1190–1160 cm^{-1} (see Figs. 1a and Part II, 1a). The narrowness of the bands at once reveals the fact that they are "parallel" bands, and that the change of electric moment is along the C−I axis (i.e., there is no change in the energy of rotation about the C−I axis, since on account of the small moment of inertia of the methyl group, this would give rise to wide rotational structure). The absence of any very pronounced

[10] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).
[11] A. B. F. Duncan, J. Chem. Phys. **3**, 384 (1935).

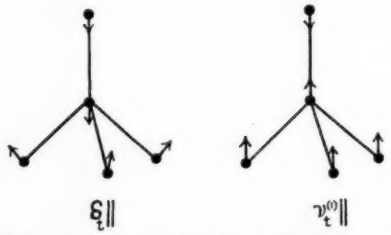

FIG. 3. The $\delta_t||$ and $\nu_t^{(1)}||$ modes of vibration of the alkyl halides.

shading of the bands to the red or the violet indicates also that the moment of inertia has been little altered by the electronic transition. The frequency separation (~1190 cm^{-1}) occurring in the progressions, has been attributed to the totally symmetrical deformation frequency of the methyl group $\delta_t||$ (see Fig. 3), which has a value of 1252 cm^{-1} in the ground state. This vibration, which just represents the motion of the hydrogen atoms perpendicular to the C−H bonds, occurs in all alkyl compounds with slightly modified values. Its appearance in the ultraviolet absorption spectra of acetone, acetaldehyde, the methyl halides, etc., at first lead to the suggestion that the excitation occurred in the alkyl part of the molecule. This hypothesis is however no longer tenable.

The existence of three or four members of the above progressions indicates that there has been an appreciable change in the potential surface in the alkyl group. This is supported by the diminution of the frequency to 1100 cm^{-1} as compared with its value in the ground state (1252 cm^{-1}). In the D state only two members of the $\delta_t||$ progression were observed, namely the main band D_1 and a very much weaker band lying about 1230 cm^{-1} to the short wave-length side of it. This separation is very close to the value of $\delta_t||$ in the ground state. Thus the change in the potential surface corresponding to this electronic transition must be extremely small, a fact which is consistent with the weakness of the band. Little can be said about the bands in the region of predissociation (1650–1400A). However it is quite certain that as we approach the ionization limit the intensity of the vibration bands diminishes to zero. Thus the excitation only causes much vibration when the excited orbit is of the same dimensions as the molecule.

The same phenomenon is observed for the bands of methyl bromide and methyl chloride. The B and C states of these molecules consist of diffuse bands which exhibit frequency differences of ~1100 cm^{-1}.* However the D states are sharp (see previous sections of this article) and are accompanied by relatively weak vibrational bands. The strongest of these are separated from the main bands by 1260 cm^{-1} in the case of the bromide, and 1320 cm^{-1} in the case of the chloride. These differences are undoubtedly to be associated with a vibration of the type $\delta_t||$ (by reason of the selection rules, their magnitudes, etc.). We therefore have the following table of the values of the $\delta_t||$ frequency in the various states. (X is the ground state.)

State	CH_3I	CH_3Br	CH_3Cl
B	1090	~1100	~1100
D	1230	1260	1320
X	1252	1305	1355

Thus in the higher excited states and probably also in the ion the vibration frequency is not greatly different from what it is in the unexcited molecule. This is consistent with the fact that the vibration is confined to the methyl group and that the excitation is that of a non-bonding electron from the halogen atom.

Another type of vibration which one expects to appear fairly strongly in the excited electronic states is the totally symmetrical valence frequency of the C−X bond $\nu_t^{(1)}||$ (see Fig. 3). In the case of methyl iodide, Henrici[12] found that one quantum of this type of vibration accompanied each of the members discussed in the previous paragraph. It appears at much less strength than the CH_3 deformation frequencies and has values ranging from 450 to 520 cm^{-1} as compared with 532 cm^{-1} in the ground states.* No analogous bands appear in the B and C states of either the bromide or the chloride. In the case of the D band of the bromide (66,025 cm^{-1}), a weak accompanying band, lying 470

* There seems to be some slight disagreement between the measurements of the long wave-length bands of methyl bromide given by Herzberg and Scheibe and those given by Henrici. The author's measurements agree most closely with those of Herzberg and Scheibe. Also it is now clear that their classification of the bands is the correct one.

[12] A. Henrici, Zeits. f. Physik **77**, 35 (1932).

* One peculiar phenomenon occurring in both the B and C states of methyl iodide is that the band corresponding to the superposition of one quantum of each of the two types of vibration discussed above, is apparently very weak.

cm^{-1} to the short wave-length side of it, is probably to be attributed to this type of vibration. However in the *D* system of the chloride no similar band, which could be assigned to a vibration in the C−Cl bond, was found.

Two perpendicular types of vibration have been found to occur weakly in the *B* and *C* states of methyl iodide (see references to Scheibe, Povenz and Lindstrom, and Henrici and Grieneisen). These exhibit the wide rotational structure and periodicity of intensity characteristic of the rotation of a CH_3 group. Other very weak bands which have not been assigned are most probably to be attributed to "double" molecules. On account of the dipole character of the molecules they tend to stick together in a "head to tail" arrangement. This results in the appearance of some frequency differences which are much smaller than can be attributed to single molecules.

The remarks made above in connection with the methyl halides will be supported and carried a stage further in Part II where the higher alkyl halides will be considered.

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The Far Ultraviolet Absorption Spectra and Ionization Potentials of the Alkyl Halides. Part II

W. C. PRICE,* *The Physical Chemistry Laboratory, Cambridge, England*

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The absorption spectra of the ethyl and higher halides have been examined in the region 2000–1000A. It has been found that they are essentially similar to those of the methyl halides. The ionization potentials of ethyl iodide are given as 9.30 and 9.88 volts and those of ethyl bromide as 10.24 and 10.56 volts. The ionization potentials of the higher halides cannot be determined exactly because of the presence of continuous absorption from the C−C and C−H bonds, and of the diffuseness of the bands themselves. However there is strong evidence that the ionization potentials of consecutive members of the homologous series diminish asymptotically to a limiting value, the diminution from methyl to ethyl being by far the greatest. A comparison of the way the ionization potentials diminish and the dipole moments of the carbon-halogen bonds increase as we ascend the homologous series indicates a definite connection between the two phenomena.

THE ABSORPTION SPECTRUM OF ETHYL IODIDE

IT is extremely interesting to study the absorption spectra of the higher alkyl iodides in relation to the spectrum of methyl iodide because it is known from the analysis of the latter that the excitation is confined to the halogen part of the molecule. A comparison of its spectrum with those of the higher iodides will indicate what effect the increase in size of the alkyl group has on non-bonding $p\pi$ electrons attached to the halogen atom. The spectrum of ethyl iodide is particularly important in this connection because it happens that the bands are sufficiently sharp to be followed right up to the two limits. The two ionization potentials of the molecule can thus be determined accurately and indisputably, and may then be compared with the values obtained for methyl iodide. The spectra of most of the other alkyl halides are diffuse near the limits and also tend to be completely obscured by relatively strong continuous absorption from C−C and C−H bonds. The deductions concerning them have therefore to be made from comparatively few bands.

The absorption spectrum of ethyl iodide in the region 2020–1700A was first obtained by Scheibe, Povenz and Lindstrom.[1] In this region it is remarkably similar to the spectrum of methyl iodide with, however, certain notable differences. The bands have a more complex fine structure due to added vibrational degrees of freedom.* The B_3, B_4 and C_3, C_4 bands are

* Senior 1851 Exhibitioner, Trinity College.

[1] G. Scheibe, F. Povenz and C. F. Lindstrom, Zeits. f. physik. Chemie **B20**, 283 (1933).

* It is worth while noting that the additional vibrational structure is most probably due to deformation frequencies of the C−C bond. Thus in the spectrum of ethyl iodide, the

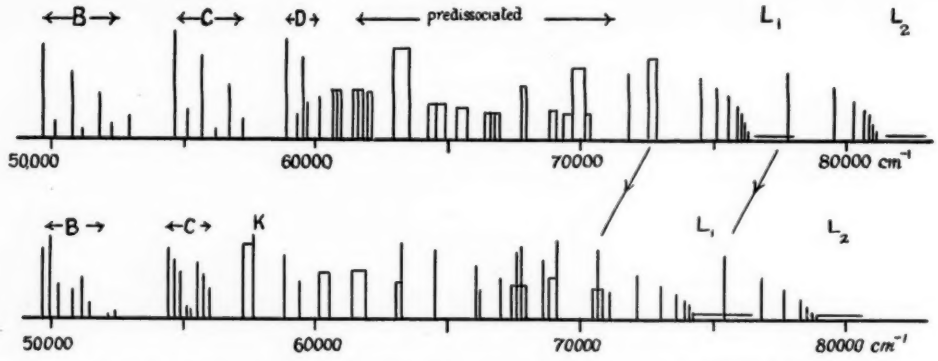

FIG. 1. Diagrams of the absorption spectra of CH_3I (upper) and C_2H_5I (lower).

greatly diminished in intensity and a new diffuse band K of very considerable strength appears in the short wave-length end of this region. Diagrams of the spectra of methyl and ethyl iodide are shown in Fig. 1. Only the very strongest bands have been marked. Where these are discrete they have been represented by single lines, while the diffuse bands are denoted by rectangles. The diagram shows that the bands of ethyl iodide come to two limits, one around 75,400 cm^{-1} (1330A) and the other around 80,100 cm^{-1} (1250A). These are to be compared with the limits of methyl iodide at 76,830 cm^{-1} (1330A) and 81,990 cm^{-1} (1220A).

The bands of ethyl iodide near the series limits are not so complex as the corresponding bands of methyl iodide, i.e., there are not so many electronic series approaching each limit. (N.B. This is not brought out in the diagram.) Most of the intensity is confined to one series for each limit. The Rydberg formulas which the upper members of these series conform to, are:

$$\nu_0^n = 75{,}380 - R/(n+0.80)^2,\ n = \cdots 4, 5, 6 \cdots, \quad (7)$$

$$\nu_0^n = 80{,}080 - R/(n+0.80)^2,\ n = \cdots 4, 5, 6 \cdots. \quad (8)$$

The limits correspond to ionization potentials of 9.299 and 9.883 volts with a probable error of about 0.005 volt. It is therefore clear that a difference of about 0.6 volt is maintained in going from methyl to ethyl iodide though the ionization potentials of the latter are diminished by 0.2 volt relative to the corresponding ones in methyl iodide. The diminution may probably be looked upon as a charge transfer effect due to the presence of the additional CH_2 group. This apparently causes a further accumulation of negative charge on the iodine atom and thus reduces the ionization potentials of electrons surrounding it. It will be treated later.

It seems quite certain that the B and C bands of methyl and ethyl iodide are to be attributed to similar electronic transitions because they occur at almost the same wave-lengths. The correlation of the shorter wave-length bands is not so obvious. However it is felt safe to correlate the bands in series (1a) and (2a) of methyl iodide with the corresponding bands of series (7) and (8) of ethyl iodide. The evidence in support of this is that the series are the strongest which appear in the spectra; that they have closely the same variable terms in the Rydberg formulas (and consequently approximately the same term values), and that they exhibit the same ΔV separation of about 0.60 volt. A shift to the red of about 30A of the spectrum of methyl relative to that of ethyl iodide would bring the strongest bands near the limits into coincidence. It is difficult to establish the correlation in the region of predissociation. The presence of a strong band of ethyl iodide at 1745A which does not possess a related band at the same wave-

deformation (bending) frequencies of the C−H and C−C bonds are strongly excited whereas the valence frequency of the C−I bond hardly appears at all, in spite of the fact that an electron from the iodine atom is excited. The same thing occurs in the spectrum of acetone where the excitation is of a non-bonding electron which is initially localised on the oxygen atom. Here again the C−C and C−H deformation frequencies appear strongly while the C−O valence frequency is only weakly excited, if at all. The frequencies appearing in the absorption spectra of acetone and formaldehyde which are around 1000–1300 cm^{-1} must be ascribed to a C−H bending frequency and not to a C−O valence frequency as was at one time thought.

TABLE I. *Table showing the observed and calculated frequencies of the C_2H_5I bands of series (7) and (8).*

	Series (7)		Series (8)		Observed
n	ν obs.	ν calc.	ν obs.	ν calc.	Separation
4	70620	70617	75380	75317	4760
5	72110	72118	76800	76818	4690
6	73010	73007	77710	77707	4700
7	73570	73576	78280	78276	4710
8	73960	73963	78650	78663	4690
9	74240	74237	78930	78938	4690
∞	—	75380	—	80080	4700

The bands $n=2$ and 3 are diffuse and deviate somewhat from the formula.

length in methyl iodide is the first indication that the ionization potential of C_2H_5I is less than that of CH_3I. This band, which is denoted as the *K* band by Scheibe, Povenz and Lindstrom, has "come up" from shorter wave-lengths as a result of this shift to the red.

It thus appears that there is one class of bands in the spectrum of ethyl iodide which suffer little or no shift relative to those of CH_3I and another class which are shifted very considerably. The bands which form series converging to the ionization potentials certainly belong to the latter class. Mulliken[2] has remarked that the simplest interpretation of the *B* and *C* levels of the alkyl halides is that they correspond to $6d\pi$ iodine orbitals and states that they should not be greatly altered by the change from CH_3I to C_2H_5I, etc. These orbitals correspond to an anchor ring type of distribution perpendicular to the C—I axis. Thus they do not greatly penetrate the alkyl part of the molecule and are therefore not affected much by changes in it.

Mulliken has also suggested that the upper levels of the long wave-length continua of methyl and ethyl iodide are the "6*s*" orbitals of iodine. Now as has been previously stated the first members of the Rydberg series which have been found here, seem to lie in these continua. It is therefore possible that the orbitals of the upper states of the series correspond to "*ns*" orbitals of iodine. If this is so we have some explanation of the large shifts to the red of the bands classified into the series, since on account of the spherical distribution of the excited orbitals they penetrate considerably into the alkyl group and are therefore strongly affected by it.

[2] R. S. Mulliken, J. Chem. Phys. **3**, 514 (1935).

The absorption spectra of iso-propyl, normal and tertiary butyl iodides have also been obtained. As is to be expected from the previous interpretation, very little shift is suffered by the *B* levels. However the bands at shorter wave-lengths (i.e., below 1700A) are shifted quite appreciably to the red with respect to the corresponding bands of methyl iodide, though the shift to the red relative to the bands of ethyl iodide is very small. Thus it is to be expected that the ionization potentials of these molecules are only slightly less (i.e., a few hundredths of a volt) than those of ethyl iodide. The diffuseness of the bands and continuous absorption from the C—C bonds prevents exact values of the ionization potentials being obtained. It is well to note that we have here the first evidence of the decrease in the term values of the electrons round the "active" atom for the consecutive members of a homologous series. The fact that this decrease is comparatively large in going from methyl to ethyl iodide and smaller for subsequent increases of the alkyl group can probably be linked up with the well known anomalous behavior of the first members of homologous series.

The Alkyl Bromides

All the bands of ethyl bromide are very diffuse compared with those of methyl bromide. The *B* bands begin around 1770A and thus apparently suffer a shift of 15A towards shorter wave-lengths relative to the corresponding bands of methyl bromide. The *C* bands suffer a somewhat smaller shift (~10A). However apart from this initial anomaly the *B* and *C* bands remain at closely the same wave-length for all subsequent increases in the alkyl group. The *D* system and all systems occurring at shorter wave-lengths than *B* and *C* are, however, shifted very considerably to longer wave-lengths. For instance, the *D* band which occurs in methyl bromide at 1515.5A, becomes a rather diffuse band at 1571A in ethyl bromide, thus suffering a shift of ~66A (0.29 volt) to the red. (This band is very easily identified as it is the first strong absorption band on the short wave-length side of the *B* and *C* systems.) Though the bands of ethyl bromide are too broad and diffuse for accurate measurements to

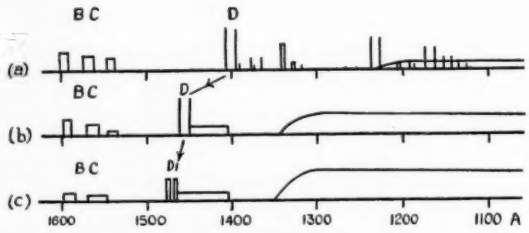

FIG. 2. Diagrams of the absorption spectra of (a) CH_3Cl, (b) C_2H_5Cl and (c) $n-C_3H_7Cl$.

be made on them, it is possible by superimposing the plates of CH_3Br and C_2H_5Br to set up a one to one correspondence of the bands of these two molecules. In order that the bands close to the two limits should line up together, it was found necessary to shift the spectra relative to each other by about 29A. In this particular region this shift amounts to 0.25 volt. The ionization potentials of ethyl bromide are thus 10.24 and 10.56 volts (i.e., 0.25 volt less than the values given for methyl bromide in Part I). These values cannot be considered to be very accurate as the presence of continuous absorption from the C−C and C−H weakens the background and makes the observation of the higher bands extremely difficult. The probable error is considered to be about 0.02 volt.

The absorption spectrum of *n*-butyl bromide has also been obtained. It is found that while the *B* and *C* bands remain in the same positions as in ethyl bromide, the *D* bands shift to the red by about 15–20A. A great deal of this shift is probably due to the increasing breadth and diffuseness of the band. In fact the bands at shorter wave-lengths suffer shifts of only about 5A. Strong continuous absorption from the C−C bonds make the estimation of the ionization potentials impossible. It is considered, however, from the shifts of the shortest wave-length bands observed, that the ionization potentials of *n*-butyl bromide can only be a few hundredths of a volt less than those of ethyl bromide.

THE ALKYL CHLORIDES

The *B* and *C* bands of the alkyl chlorides are extremely diffuse. They fall in the region 1610–1540A (see Fig. 2) and suffer very little alteration in wave-length in passing from methyl chloride to the higher members of the homologous series. Now it has been mentioned in connection with methyl chloride that the *D* bands, which are very strong bands at 1406 and 1394A, are the first members of the strongest Rydberg series going to the ionization potentials of this molecule. The variation in the position of these bands with increase in the alkyl group will serve as an indication of the changes in the ionization potentials. (Experience shows that the ionization limits will be located about the same distance to the short wave-length side of these bands.) The spectra of methyl, ethyl and *n*-propyl chloride are shown in Fig. 2. It can be seen that the main electronic doublet, characteristic of the alkyl chlorides ($\Delta V=0.08$ volt), persists in going from methyl to ethyl chloride. However the bands are shifted to the red by ~59A (1465–1406A) or 0.36 volt. Judging from what happens in the bromides, the diminution in the ionization potentials will be somewhat less than this, i.e., ~0.32 volt (not greater as was originally thought).

The spectra of propyl, iso-propyl and several varieties of butyl, amyl and allyl chlorides have been obtained. They become increasingly diffuse with increase in molecular weight and the strength of the continuous absorption from C−C and C−H bonds is correspondingly increased. It was found that the *B* and *C* bands for all these substances remain at approximately the same wave-lengths. However the *D* bands suffer small decreasing shifts to the red and eventually reach a limiting position ~1495A. Little difference could be detected between the *n*, iso, secondary, tertiary, etc., varieties except for the rough generalization that the closer the C−C were to the chlorine atom the greater the shift to the red. It should be noticed that by far the greatest shift towards longer wave-lengths occurs in the change from the methyl to the ethyl halide, i.e., in placing *one* C−C bond next to the C−X bond, and that the shifts of iso-propyl and tertiary butyl halides are not twice or three times the first shift, as might perhaps be expected, but only slightly greater than it.

It is interesting to note that the experimental results of this work seem to indicate a relation between the way the ionization potentials of the alkyl halides decrease asymptotically to a mini-

mum and the way their dipole moments increase to a maximum in going up a particular homologous series. The change of both properties is greatest in going from the methyl to the ethyl compound and very much smaller for subsequent increases in the alkyl group. As both phenomena presumably depend on the accumulation of negative charge on the halogen atom such a correlation is not unexpected. Unfortunately, shortness of time has interfered with a thorough treatment of this subject.

In conclusion the author wishes to express his indebtedness to Dr. W. G. Penney for his very valuable criticisms and to Professor J. E. Lennard-Jones for some very helpful discussions. It should also be stated that the earlier part of the work was done at The Johns Hopkins University.

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Fluorescence of Chlorophyll in Its Relation to Photochemical Processes in Plants and Organic Solutions

J. FRANCK AND R. W. WOOD, *The Johns Hopkins University, Baltimore, Md.*

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The intensity of the fluorescence of chlorophyll in organic solutions in its relation to photochemical reactions can be explained by the assumption that the excited chlorophyll, which is free from adsorbed molecules, has a small probability of reemitting light as fluorescence, and a greater probability of predissociating into a hydrogen atom and monodehydrochlorophyll. In the presence of oxygen the product of dissociation will react with it. If acceptor molecules (*RH*) for oxygen are added to the solution, they will take over the excitation energy and protect the chlorophyll against oxidation, while they themselves will be oxidized; the first step being the dissociation of *RH* into *R* and *H*. The energy transfer may take place by impact of the second kind or as an intramolecular energy exchange within a complex molecule *H Chph RH* which will dissociate into *H Chph R* and *H*. The formation and consumption of the complex radical *H Chph R* is responsible for the change of intensity of the fluorescence with the time of irradiation which occurs in the presence of oxygen and some acceptor molecules in organic solutions. Analogous intensity time relations have been found and qualitatively described by Kautsky and his co-workers for the fluorescence of living leaves in the presence of oxygen. Quantitative measurements of these curves under various conditions form the experimental part of this paper. All observations can be interpreted by the assumption that not only photosynthesis but also photoxidation of organic substances adsorbed to chlorophyll takes place in the plant. The hypothesis is suggested that photoxidation is responsible for the so-called light saturation of photosynthesis in living plants.

INTRODUCTION

THE intensity of the fluorescence of living leaves has, as Kautsky[1] and his co-workers have shown, a complicated dependence on the time of irradiation if oxygen is present, this relation obviously having something to do with the velocity of photochemical reactions which occur in the plant. Kautsky proposed a theory which directly connected these observations with the process of photosynthesis, but Gaffron and others[2] published objections to his assumptions. One of the present authors formerly thought that the shape of the observed curves could be explained by the hypothesis that the chlorophyll must first go over into monodehydrochlorophyll by a photochemical reaction with oxygen before photosynthesis can start, but Gaffron, Gaffron and Wohl and Stoll[3] have shown that this hypothesis also is in disagreement with more recent observations, and in the course of this paper other objections to this hypothesis will be mentioned. A satisfactory explanation for the fluorescence-time relations has, therefore not been given so far, and Kautsky's careful observations while interesting, are only qualitative and

[1] Hans Kautsky, A. Hirsch and F. Davidshoffer, Ber. **65**, 1762 (1932); Hans Kautsky, A. Hirsch and W. Flesch, Ber. **68**, 152 (1935); Hans Kautsky, Biochem. Zeits. **274**, 423; **274**, 435 (1934).

[2] J. Franck and H. Levy, Naturwiss. **23**, 226 (1935); H. Gaffron, Naturwiss. **23**, 528 (1935).

[3] Gaffron, reference 2; H. Gaffron and K. Wohl, Naturwiss. **24**, 81 (1936).

therefore not sufficient for the analysis of the processes. On this account it seemed worth while to reinvestigate the whole problem of the fluorescence of chlorophyll and its relation to photochemical processes in leaves and in organic solutions.

Yield and Quenching of the Fluorescence in Organic Solutions

Studies of the fluorescence of chlorophyll in organic solutions, indicate the presence of a polyatomic molecule in which a predissociation process or quenching processes compete with the reemission of light. If irradiated with light corresponding to the three absorption regions of chlorophyll in the red, blue, and ultraviolet, it reemits red light with a small efficiency. In solutions which are supposed to be inactive in relation to the excited chlorophyll molecules, the maximum yield for fluorescent light is of the order of 10 percent.[4] In the absence of oxygen a short and weak afterglow can be observed. The fluorescence can be quenched by addition of substances such as oxygen, benzidine and iodine salts, which take up the excitation energy by impacts of the second kind.[5] The quenching by oxygen is small, an amount which corresponds to a 200 mm pressure reducing the intensity by one half, while the afterglow vanishes entirely. For benzidine and NaI the curves of concentration plotted against the intensity of fluorescence are hyperbolas as expected from their analogy to the curves obtained with fluorescent gases.

Connection between Photochemical Processes Induced by Chlorophyll and Its Fluorescence in Organic Solutions

The only photochemical processes known to be induced in organic solutions by chlorophyll are photoxidations.[6] Chlorophyll may be oxidized itself or may sensitize the oxidation of acceptor molecules for oxygen. On the other hand even in the absence of oxygen the fluorescence is weak. In solutions which are supposed to be stable in relation to excited chlorophyll and free from oxygen, 90 percent of the absorbed energy is dissipated and only 10 percent reemitted. Two explanations are possible. We may assume that the molecules of the solvent are less stable than formerly assumed and consume the energy for a dissociation process, the recombination which follows causing the afterglow as chemiluminescence. The second and more probable possibility is that the chlorophyll itself is not stable and may dissociate. Again the recombination will be responsible for the afterglow. The only dissociation process of chlorophyll which seems energetically possible if red light is absorbed is the splitting off of one of the two loosely bound hydrogen atoms whose presence the chemists have proved.[7] A reemission of 10 percent of light indicates that the photochemical process does not take over the energy immediately after the act of absorption but allows a relatively long lifetime of the excited state. The first hypothesis would require that only a very small fraction of all impacts with the solvent are effective and the latter, that the photolysis of the chlorophyll itself takes time. For a polyatomic molecule such as chlorophyll (molecular weight >1000) this behavior is to be expected; the spontaneous disintegration should occur a relatively long time after the absorption act, because time elapses before the very complicated relative movement of the atoms in the molecule produces the critical constellation of the particles and a suitable energy-distribution for dissociation.[8] The time lag will vary with the nature of the neutral solution because all molecules which surround the excited chlorophyll contribute to the complexity of the molecular system, their influence depending on the forces which couple them to the chlorophyll permanently or for the time of the impacts.

The addition of a small amount of oxygen causes a photoxidation of chlorophyll if other acceptors for oxygen are absent. The oxidation may take place as a result of impacts between excited chlorophyll and oxygen, but if one accepts the predissociation of chlorophyll, the

[4] A. Prins, Nature **135** (1935).
[5] J. Franck and H. Levi, Zeits. f. physik. Chemie **B27**, 409 (1935).
[6] See for instance H. Gaffron, Biochem. Zeits. **264**, 251 (1933) and K. Noack, Zeits. f. Bot. **17**, 481 (1925).
[7] H. Fischer, J. Chem. Soc. 245 (1934); A. Stoll, Naturwiss. **20**, 955 (1932).
[8] J. Franck, H. Sponer and E. Teller, Ges. d. Wiss. Göttingen, 1929.

main oxidation should occur by the reaction of oxygen with the products of the decomposition, and the recombination, thus hindered by oxygen, abolishes the afterglow.

If acceptors for oxygen are present, chlorophyll will be protected against oxidation, while the acceptors are photoxidized with a good quantum yield,[7] the protection occurring by seizure of the excitation energy of the chlorophyll before it reacts itself. The energy taken up by the acceptors will be used for a decomposition of these molecules and the products of dissociation will react with oxygen. The transfer of the energy to the acceptor molecules may take place by normal impacts of the second kind (as in benzidine, where the quenching is connected with the concentration by a hyperbolic curve) or while the acceptor is adsorbed on the chlorophyll forming a loosely bound complex. In this case one has a high quantum yield even if the concentration of the acceptor is small. The formation of such a complex also offers an explanation for cases in which the addition of the acceptor to be oxidized with a high quantum yield does not noticeably quench the intensity of the fluorescence and may even raise it somewhat. We may mention the photoxidation of isoamylamin as an example.[9] For the sake of simplicity we will use for an adsorption complex between chlorophyll and an acceptor the symbol *H Chph RH*. The first step for the oxidation of *RH* induced by light absorbed by chlorophyll will then be expressed by the equation

$$H\ Chph^*\ RH \rightarrow H\ Chph\ R + H.$$

The question whether the addition of *RH* will raise or lower the intensity of the fluorescence is then identical with the question whether the complex *H Chph* RH* has a longer time-lag between light absorption and chemical reaction then *H Chph** surrounded merely by the molecules of the solution. We have again to distinguish between the possibility that *H Chph** may react with the molecules of the solvent or may predissociate. On the first assumption the formation of *H Chph RH* can only then raise the fluorescence if it overcompensates the use of the excitation energy for the dissociation of *RH* by shielding off from the *Chph* the impacts of the second kind of the solvent. If, on the other hand, we assume the occurrence of spontaneous decomposition of *H Chph** we have, in order to explain the rise of the fluorescence, to ascribe to *H Chph* RH* a longer time-lag until predissociation occurs, as for *H Chph**, in spite of the two possible predissociation processes in the complex, and only one in the *Chph* free from *RH*. This is possible because the greater complexity of the system *H Chph RH* compared with *H Chph* tends to increase the time-lag between adsorption and predissociation.

[9] H. Kautsky, Ber. **68**, 152 (1935).

Changes of the Intensity of Fluorescence with the Time of Irradiation in Organic Solutions

According to results of Franck and Levi,[5] weak alcoholic or acetonic extracts of leaves irradiated with strong light in the presence of oxygen show a dependence of the intensity of fluorescence on the time of irradiation similar to that which Kautsky found for the living leaves, the essential difference being the much slower progress of the processes in the solutions. Here the intensity of the fluorescence is weak at the very beginning of irradiation, rising quickly, to a maximum after 20–30″ and then fading away in a few minutes (exponentially) almost to the low initial value. A repetition of the curve is possible only after a longer repose in the dark. Without oxygen the fluorescence shows practically a constant intensity, which is somewhat higher than the intensity at the beginning and end of the curve with oxygen, but lower than its maximum. The solution contains not only the chlorophyll but also other substances which are known to be acceptors for oxygen and easily photoxidized by chlorophyll. The photoxidation being the only photochemical process which occurs in these solutions, one must explain the shape of the curves by connecting the fluorescence-time relations with the progress of the photoxidation. According to the assumptions made above some substances when photoxidized will give, with the chlorophyll a complex of the form *H Chph RH*. We have to assume that the substances extracted from leaves belong to this class, inasmuch as the reaction proceeds quickly in spite of the low concentration in which these substances are present in the solution. The

complex *H Chph* RH* has a relatively small chance of reemitting light, most of the excited complex molecules reacting photochemically by the process

$$H\ Chph^{*}\ RH \rightarrow H\ Chph\ R + H.$$

The complex radical *H Chph R* produced by the light will be present only in a small concentration since it will be quickly consumed by the attack of oxygen and removal of the oxidized substance from chlorophyll. But the small amount of *H Chph R* may contribute considerably to the intensity of the observed fluorescence, as this radical must have a much greater ability to fluoresce than the original complex. After the splitting off of the hydrogen atom from *RH* the only possibility of using the excitation energy for photochemical purposes in the complex-radical *H Chph R* is the splitting off of the hydrogen atom from the chlorophyll and this process has, if it occurs at all, a small probability on account of the complexity of the molecular system. After the consumption of *RH* the *H Chph* liberated from the complex remains in the solution. This substance will again be a less effective reemitter than *H Chph R*, since if predissociation occurs this process will take place more rapidly as the molecular system is now simpler than the adsorption-complex. If there is no predissociation, *H Chph* will be inefficient for fluorescence because it has lost the protection against impacts of the second kind by the loss. The change of the intensity of the fluorescence with time is then an indicator of the change of concentration of *H Chph R* with time. The first rise of the curve is caused by the production of *H Chph R* by the light. The maximum occur in a short time since the lifetime of the radical is short, in consequence of which the equilibrium between production and consumption of *R* will be quickly reached. If an inexhaustible amount of *RH* were available, the intensity would remain constant after the establishment of equilibrium. This not being the case the slow decay is proportional to the consumption of *RH* by photoxidation.

Direct measurements of the lifetime of *R* and the dependence of the decay on the amount of *RH* present in organic solutions are planned. They should show the same results as the analogous experiments described below on the fluorescence of living leaves.

The Time-Intensity Relation of the Fluorescence in Leaves Indicates Photoxidation But Not of the Chlorophyll Itself

As was mentioned in the introduction, the starting point for this research was Kautsky's observations on the dependence of the fluorescence of chlorophyll in living leaves on the time of irradiation in the presence of oxygen. The general shape of the curve (which alone was known until now) is the same as that described for the solutions, which led one of the authors to assume that also in living leaves a photoxidation was responsible[10] for the behavior of the fluorescence. But the specific assumption that chlorophyll itself will be partially oxidized in going over to monodehydrochlorophyll in the plant and that this process is a necessary condition to start photosynthesis, is wrong. To the evidence given in the meantime by Gaffron and Gaffron and Wohl[3] (see also Stoll) we can add as a result of a few observations that a strong illumination of living leaves does not produce a considerable change of the absorption spectrum in the first few seconds of irradiation. This, however, should happen if all of the chlorophyll was transformed into monodehydrochlorophyll. In the special case of chlorophyll a splitting off of one of the loosely bound hydrogen atoms should change greatly the absorption spectrum according to the well-founded theories of Hückel and Pauling, as was pointed out to us by Dr. Corwin, who made also other helpful suggestions. The question now arises, which substances will be photoxidized in living leaves at the beginning of an illumination period, and what has this photoxidation to do with photosynthesis? Quantitative measurements of the time-intensity curves of fluorescence should offer much better information than Kautsky's qualitative ones, which however proved of great value to us in our choice of different experimental conditions, and our measurements are in accordance with his observations.

[10] J. Franck, Naturwiss. **23**, 221 (1935); Chem. Rev. **17**, 433 (1935).

General Experimental Procedures for Measuring the Time-Variation of Fluorescence of Living Leaves

Our arrangement for measuring the fluorescence of leaves was a very simple one. We excited the fluorescence with blue light emitted by a 750 watt tungsten lamp filtered through cuprammonium and focused by two large condenser lenses, on the under side of the leaf. A total-reflecting prism was used to deflect the converging cone of rays through a right angle in order to permit observation of the fluorescence in a direction perpendicular to the surface of the leaf. The blue patch of light on the surface of the leaf was observed through a red filter and the red fluorescence measured with a small photometer, constructed by Dr. Pfund, which allowed quick and exact comparisons with a beam of another source of red light whose intensity could be varied. The calibration curve of the photometer was obtained in the usual way with an optical bench. The red filter cut off all blue light reflected and scattered by the leaf so that only the intensity of the red fluorescent light was measured.

Measurement of the Decay of Fluorescence

The main shape of the curve—light intensity as a function of time—obtained in normal air and room temperature is in accordance with Kautsky. A steep rise of the fluorescence to a maximum reached in about one second is followed by a much slower decay. The decay varies a little if different kinds of leaves are used but is in the case of most of the leaves a perfect exponential function (with an asymptotic value different from zero); the decay of the intensity taking place in the course of $\frac{1}{2}$ to 1 minute could after a little practice be followed directly with the photometer and a stop-watch.

Measurement of the Rise of the Curves

We made no attempt to measure the steep rise of the curve at the beginning of an illumination period limiting ourselves to measuring the initial intensity and the intensity at the maximum. To obtain the initial value a flat metal disk of 12 cm diameter was covered with large pieces of leaf cuttings attached by glue and set in rotation by a motor. While the disk was revolving a narrow spot near the rim was illuminated with blue light. The time of exposure of each part of the leaf at the rim in the course of one revolution was only a few thousandths of a second, this short illumination not changing the conditions in the leaf, especially if the intensity of the impinging light is reduced. The fluorescence measured under these conditions can be accepted as identical with the initial fluorescence of a stationary leaf if it can be shown that the periodic repetition of the illumination is not a disturbing factor. This was controlled by longer sets of observations, which showed, that although a slow change of the fluorescence with time occurred (the general shape being the same as with constant illumination) the rate of change was so much smaller and slower that this effect could be neglected in the case of rapid observations.

Measurement of the Recovery Curves

In accordance with Kautsky's results it was found impossible to repeat the measurements with the same result, directly after a prolonged illumination, a long rest in the dark being necessary to restore the conditions as at the start. We measured the recovery in the dark as a function of time in the following way. After the final state of an extended illumination was reached, the leaf was rested in the dark for different intervals of time and the height of the maxima of the fluorescence during a very brief illumination as a function of the time of rest in the dark was measured. The measurement of each point of the curve disturbs of course the recovery, and to make this disturbance as small as possible, it was therefore necessary to employ a very brief illumination for each measurement. After making a series of measurements, considered reliable enough to show the character of the curve, control experiments were made by setting the photometer while the leaf was resting in the dark to the value to be expected for a given time of rest and comparing only the sign of the deviations. In the majority of observations the deviations were very rare and moreover very small.

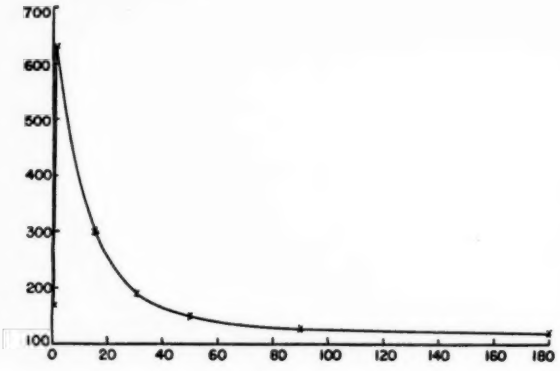

FIG. 1.

MEASUREMENT OF THE LIFETIME OF THE RADICAL *H Chph R*

In accordance with the explanation given above for the curves obtained in organic solutions, one would expect the light to produce a strongly fluorescent substance with a short lifetime, and it was possible to prove the production of this substance and to measure its life by the following procedure. Two flashes of light were applied one after another; if the first one produces a substance more able to fluoresce, the fluorescence caused by the second one will be increased by the previous illumination. The increase produced by the previous illumination will fade away if the time interval between the two flashes becomes greater. The light intensity observed at the second flash plotted against the time difference elapsed between the two flashes allows one to calculate the lifetime of the substance. The real experiment was not made with flashes but with a continuous illumination of *two* spots of the leaves near the rim of the rotating disk. For each individual revolution this is equivalent to two flashes and the time between the flashes can easily be changed by changing the distance between the two patches of light. The disk revolved with a constant speed giving a constant total duration of the illumination by the two spots of light. As sources of light we used for spot II our normal blue illumination and for spot I white light emitted by an 8-volt tungsten lamp mounted as close as possible to the surface of the rotating disk and shielded by a metal tube to avoid disturbances by scattered light. If the two patches of light are not nearer than 2–3 cm from each other this precaution is sufficient. The periodic repetition of the illumination fatigues the leaf, as was mentioned on page 11, and this influence was much greater than with the single spot of light employed before, since it was necessary to apply a much stronger illumination. The fatigue showed itself by the fact that the influence of the illumination by spot I on the fluorescence observed at spot II became smaller if the time of illumination was increased and at last vanished entirely. To avoid this disturbance the measurement for each

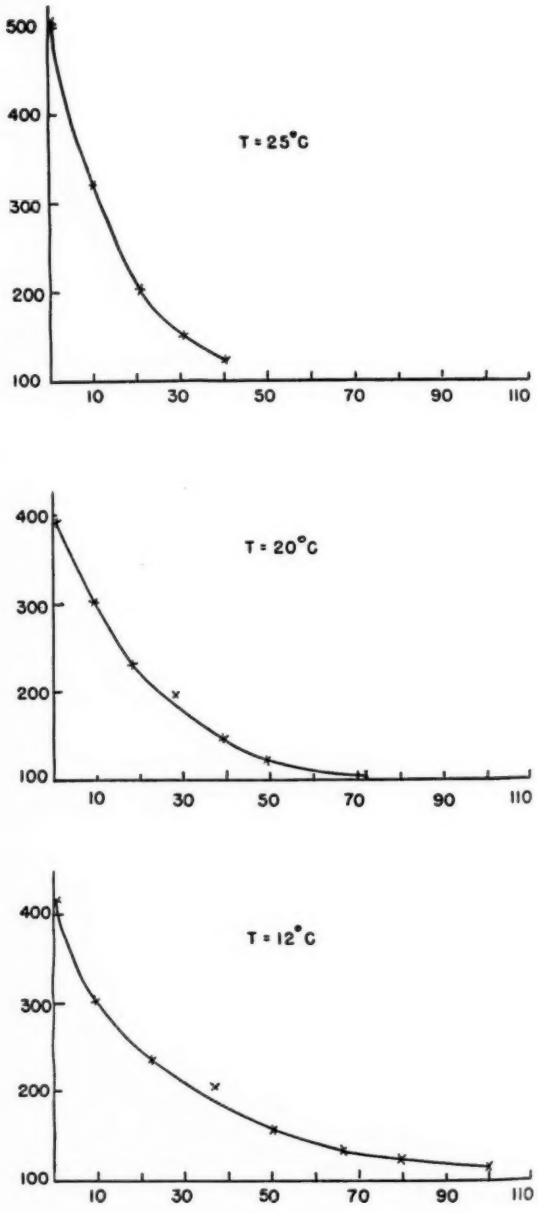

FIG. 2.

point of the curve was made with a very short exposure and the leaf allowed to recover in the dark between successive observations.

Measurement of the Influence of Different Gas Atmospheres on the Fluorescence Time Curves

Measurements on the influence of different gas atmospheres on the general shape of the curves were made with a shallow circular box of brass covered by a glass window, and rotated in the same manner as the disk, the leaf cuttings being attached to the bottom of the box. Gas was introduced through a small tube inserted in the rim of the wheel.

Measurements of the Influence of Temperature Variation on the Shape of the Fluorescence Time Curves

Our first rough measurements were made by attaching the leaf to the outer surface of a copper box filled with water at controlled temperature. This method, however, does not determine the surface temperature exactly and the final determinations were made either by immersing a test tube containing the leaf in a water bath, or by altering the temperature of the whole room.

Most of the observations were made with leaves of hydrangea or later in the winter with leaves of ficus, and several other plants (geranium, marsilia, etc.) which showed, in accordance with Kautsky, that the different plants behave in essentially the same way. The leaves were of course used only as long as they remained in a fresh condition.

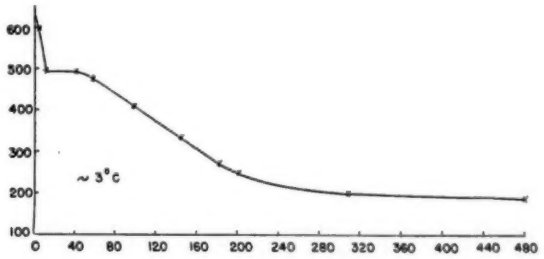

Fig. 3.

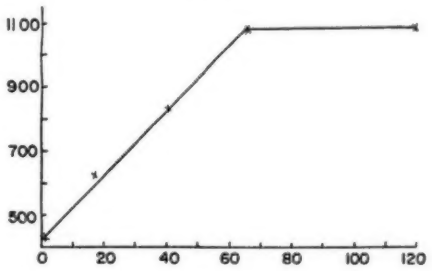

Fig. 4.

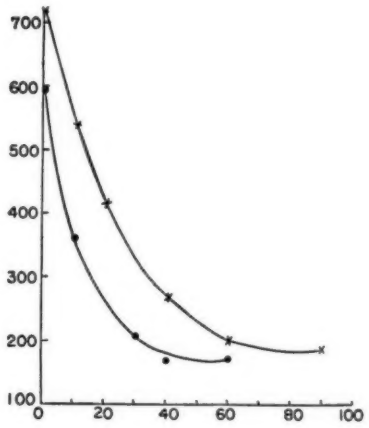

Fig. 5.

Results

In air with the normal amount of carbon dioxide the curves are as shown in Fig. 1, and, with the strong illumination employed, the intensity of the fluorescence is, always proportional to the intensity of the exciting light. The starting point has practically the same height as the asymptote reached after a long exposure, and the time constant of the exponential curves is independent of the strength of the light.

Fig. 2 shows the dependence of the decay on the temperature. The change of the time constant of the decay curves with temperatures can be interpreted by a constant temperature coefficient if one observes the curves between 25°C and 10°C. Lower temperatures gave other types of curves as in Fig. 3. The first sharp maximum cannot always be observed, and we suspect that it may be caused by temperature differences between the surface and the inner part of the leaf.

Fig. 4 shows an example of recovery curves. They are strictly linear. It seems that after the apparent equilibrium is reached (which takes the time of the order of magnitude of one minute) a very slow and small rise takes place for hours, as is indicated by the higher maximum, observed after a whole night's repose in the dark.

The dependence of the decay of the curve on the amount of CO_2 in the presence of oxygen was studied by removing with KOH the CO_2 from the air which streamed over the leaf. This treatment causing a much quicker decay of the intensity. Moreover the maximum was somewhat smaller and the fluorescence of the fatigued leaf became very weak. Fig. 5 shows two curves for a different amount of CO_2, the lower one has less CO_2, the decay is quicker and the total intensity smaller. Entirely reproducible results could only be obtained after several hours' treatment with air free from CO_2 and several illuminations and dark pauses.

Fig. 6 shows curves in a pure CO_2 atmosphere free from oxygen. Curve I shows the conditions ten minutes after the treatment with pure CO_2, Curve II half an hour later, and Curve III the final condition after several hours. For comparison purposes the normal Curve IV, obtained from the same leaf in air with the normal amount of CO_2 is given.

Observations on fluorescence as influenced by poisoning the leaves with prussic acid were made by moistening a part of the surface of the leaf with KCN solutions and the results are shown by Fig. 7. Curve 1 represents a normal leaf, curve 2

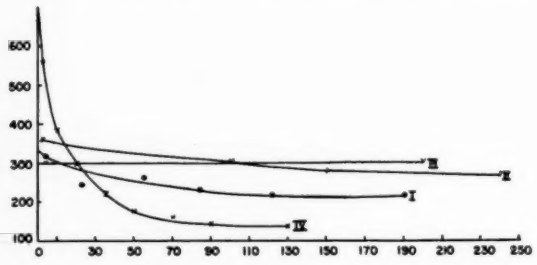

FIG. 6.

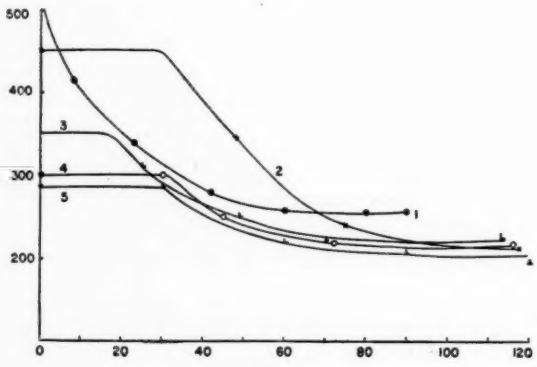

FIG. 7.

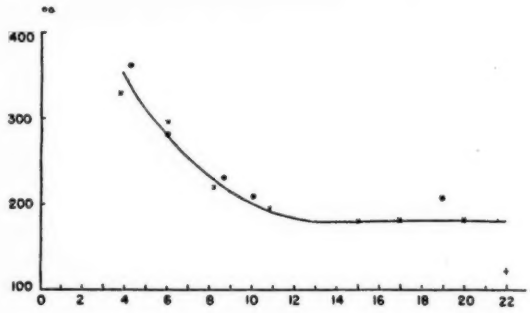

FIG. 8.

the fluorescence a short time after the poison was applied, and curves 3, 4 and 5 the influence of a stronger solution applied for longer times. The main changes are these: The fluorescence is much weaker and, while the first rise seems to be normal (not shown in the curves), the decay which follows the maximum is delayed as with very low temperatures.

Repeated applications of KCN solution followed by a ten hour repose in the dark, reduced the intensity of the fluorescence nearly to zero, and changed the color of the leaf from green to brown.

The measurements of the lifetime of the substance (*H Chph R*) by the method by the two spots of light gave results reproduced by Fig. 8. The curves obtained seem to be exponential with a half value of about 2/100 sec. The single point below the curve marked by + gives the value for the fluorescence without previous illumination. The fact that this point was always lower than the asymptotical extrapolation of the curve seems to show that the short illumination produces not only the substance with a short lifetime but causes also smaller changes which do not fade away in the time of one revolution of the disk ($\sim$ 1/6 sec.).

The time constant 2/100 sec. coincides with the time for the expiration of the Blackman reaction measured by Arnold and Emerson.[11] We expected that this coincidence was accidental because the production of the substance studied here is only detectable in unfatigued leaves after a repose in the dark, while the substance undergoing the Blackman reaction was studied by Emerson and Arnold after long periods of strong flash illumina-

[11] R. Emerson and W. Arnold, J. Gen. Physiol. 16, 191 (1932).

tion. To prove that the lifetime measured here has nothing to do with the Blackman reaction we studied qualitatively whether prussic acid influences the lifetime. The experiments showed an independence so far as the accuracy of our experiments goes. An influence which would be as great as that caused by prussic acid on the Blackman reaction would easily be detected.

Discussion

These observations on the fluorescence of living leaves are to be interpreted in the same way as the results discussed above for the fluorescence of chlorophyll in organic solutions. In both cases a photoxidation takes place sensitized by the chlorophyll. While it is not yet possible to analyze directly the substances which undergo the oxidation, a good deal of information can be gained by the discussion of the changes of the time-intensity curves of the fluorescence observed under different outer conditions. It now seems probable that in the plant the chlorophyll is present on the surface of the chloroplasts, presumably in a monomolecular layer[12] which is in contact with the aqueous solution of the surroundings. This distribution would thus be different from the one in normal aqueous solutions of chlorophyll where the dye is distributed in colloidal particles entirely built up by chlorophyll molecules. But between the condition in normal aqueous solutions and in the leaves, there seems to be this similarity that chlorophyll in actual contact with water is unable to fluoresce. In normal aqueous solutions chlorophyll does not fluoresce at all and in plants only if the chlorophyll is protected by adsorbed organic substances, especially organic acids against impacts of the second kind with water molecules. One is forced to this conclusion by the fact that all conditions which lower the percentage of chlorophyll molecules carrying adsorbed organic substances also lower the fluorescence. In contrast to the weak fluorescence of leaves in air free from CO_2 after a short illumination, there is, for a longer period of illumination a stronger fluorescence after a longer dark period in normal air. In the first case the chlorophyll will be free from CO_2 and organic substances after a short illumination while in the second it will not only be connected with carbonic acid and the intermediate products between carbonic acid and formaldehyde but also with final products of photosynthesis and of the metabolism of the plant, which may be organic acids, as for instance tartaric acid. The slower the normal breathing process in the plant, the more of these organic acids will be present and they will be in competition with the carbonic acid and intermediate products of photosynthesis for the occupation of places of attachment to the chlorophyll. The concentration of the metabolic products will therefore be high if there is a lack of oxygen or if the breathing is reduced by low temperature or by poisoning with CN. This assumption is in accordance with Gaffron's[2] explanation of the slow start of photosynthesis if oxygen is removed from the plant. He assumes a poisoning of the photosynthetic apparatus by the products of the metabolism, and a reorganization of the photosynthetic apparatus by continued illumination. According to our point of view the plant gets rid of these products by photoxidation (which again may be a chain reaction). That chlorophyll in plants is able to sensitize oxidation processes was proved years ago by the important experiments of Noack[6] who has shown that benzidin brought in contact with chloroplasts in the living plant is readily oxidized. The shape of the curves in the presence of oxygen is then interpreted as above. The beginning of the period of illumination after a dark period finds chlorophyll not only connected with products to be photosynthesized but also with organic acids from metabolism. The fluorescence will be weak because the energy absorbed will be used in part for photosynthesis and in part for the formation of *H Chph R* and *H* out of *H Chph RH*. The radical H Chph R produced by light is, as in organic solutions, responsible for the change of fluorescence with time. If the concentration of its mother substance *RH* is reduced by photoxidation, *H Chph R* will be present in a smaller concentration and the fluorescence will again become small, since *H Chph* in contact with water will suffer impacts of the second kind, and *H Chph* connected with CO_2 and the intermediate states of photosynthesis will use the energy absorbed for the process of photosynthesis. Only if the influence of strong illumination is combined with

[12] K. Noack, Biochem. Zeits. **183**, 135 (1927); Cf. C. Zirkle, Am. J. Bot. **13**, 321 (1926).

a high supply of CO_2 one observes—as one can expect—a relatively high intensity of fluorescence after an extended period of irradiation. The concentration of sugar produced by photosynthesis now becomes so high that chlorophyll combines with the decomposition products of sugar which will directly and indirectly reduce the yield of photosynthesis by photoxidation processes.

As the experiments have shown, the fluorescence at each point on the curve is proportional to the light intensity, which is in accordance with the assumptions made, since the most active substance *H Chph R* is not only produced but also consumed in proportion to the light intensity.

The main influence of lack of oxygen, of low temperatures, or the poisoning by cyanide is, as was mentioned, to raise the concentration of the products of metabolism. This fact explains the similar aspect of the curves if one of these factors is applied to the leaves. The main difference from the normal curves is that fluorescence, after attaining its maximum remains constant for a time. This is a direct consequence of the great concentration of *RH*, since the places at the chlorophyll which will become free by oxidation of *RH* will be immediately filled again with new *RH* until a considerable reduction in the concentration of *RH* has occurred. The intensity of the fluorescence as well as the shape of these curves, fits into the picture. These curves show the highest intensity if a low temperature is used. The concentration of *RH* being great and also the amount of oxygen being higher than normal, the photoxidation will produce an abnormally high concentration of *H Chph R*. Lack of oxygen together with a great concentration of *RH* as in the curves of Fig. 6 gives a smaller intensity but the fluorescence remains constant for a much longer time, corresponding to the longer time taken for the consumption of the *RH*. Prussic acid, if applied for a considerable time, produces a great reduction of the fluorescence. This has to do with a slow decomposition of the chlorophyll itself as indicated by the brown color of the poisoned leaf.

The time used for the steep rise at the beginning of irradiation is not (or may be to a very small extent) influenced by the temperature or by prussic acid. This is to be expected since there is no reason to assume that the photochemical production of *H Chph R* or the lifetime of the radical should be influenced by low temperature or HCN. The last point is, moreover, proved by direct experiments. On the other hand, with less oxygen present the lifetime should become the longer. In this connection we cannot refer to our own experiments (because we did not change gradually the O_2 amount), but Kautsky mentions that the curve rises less rapidly and has a lower maximum when less oxygen is present.

Lack of CO_2 produces a quick decay of the curves, as the lower curve of Fig. 5 indicates. We explain this fact by a quicker consumption of *RH* because the places for attachment to the chlorophyll are free, and a competition with photosynthesis does not retard the photoxidation. On the other hand there is an exhaustion of oxygen since its new production by photosynthesis is absent in this case and also the concentration of sugar and its decomposition products will be abnormally small.

The recovery curves (Fig. 4) have an interesting shape, indicating a reaction of the zero order, which means that the restitution of the higher concentration of the products of metabolism (which corresponds to the equilibrium occurring in the dark) takes place by a catalytic surface reaction. The recovery curves show, according to our interpretation the difference between the equilibrium concentration of *RH* connected with *Chph* in the dark (equilibrium between production and consumption by breathing) and in the light, being in the latter lower since here the substances are not only attacked by normal respiration but also by photoxidation.

But not only should the products of metabolism be photoxidized but also the final products of photosynthesis. One may infer that this process becomes especially important if abnormally high concentrations of these products and of oxygen occur. We suppose in contradiction to the usual assumptions[3, 11] that the so-called light saturation has to be interpreted as an equilibrium in which photosynthesis and photoxidation balance each other to a given extent. This question and others connected with the problem of photosynthesis will be discussed elsewhere.

Acoustical Studies

V. The Collision Efficiencies of Deuterium and Hydrogen in Exciting the Lower Vibrational States of Ethylene

WILLIAM T. RICHARDS, *Princeton University*

(Received July 7, 1936)

Measurements on the velocity of sound in ethylene-deuterium mixtures indicate that deuterium is less efficient than hydrogen in exciting the lower vibrational states of ethylene by a factor of about 8 per collision. This difference in behavior substantiates a previous hypothesis that the marked efficiency of hydrogen in this respect may be due to its uniquely small moment of inertia. It also appears possible, however, that the mechanics of the collision process might provide an explanation. The suggestion that hydrogen at 30°, 780 mm, and 450 kc shows dispersion due to lagging of the rotational terms, which has been justly criticized by other writers, is withdrawn.

INTRODUCTION

TWO years ago, in a communication from this laboratory, measurements on the velocity of sound in ethylene-hydrogen mixtures were reported which indicated that ethylene-hydrogen collisions were about ten times as effective as ethylene-ethylene collisions in producing transitions in the lower states of the vibrational energy of ethylene.[1] Similar measurements on deuterium-ethylene mixtures were made at once with the hope of elucidating the great efficiency of hydrogen. The results obtained were temporarily withheld from publication because two major difficulties in their interpretation appeared.

The first of these difficulties concerned the tube or apparatus-correction for velocities of sound greater than 375 m sec.$^{-1}$. This is dealt with in detail in the experimental section; the findings have invalidated our previous claim to have observed rotational dispersion in hydrogen. The second concerned the purity of the deuterium employed, and the possibility of exchange reactions at room temperature between deuterium and a glass apparatus containing nichrome oscillators and traces of adsorbed hydrogen and moisture. Since objections on both of these grounds now appear to be answerable with sufficient positiveness to give the work significance, it is submitted for publication.

[1] Richards and Reid, Nature **130**, 739 (1932); J. Chem. Phys. **2**, 206 (1934).

EXPERIMENTAL

A. Apparatus

The previously described apparatus[2] required but little modification for the present purpose. Magnetostriction oscillators, cut from nichrome steel, were mounted coaxially in cylindrical Pyrex tubes of 1 cm internal diameter, and driven by valve-tube circuits of the "electron-coupled" type. This circuit which recently came into general use, is vastly more stable than that initially recommended for magnetostriction oscillators,[3] and consequently permits greater amplification and more accurate detection of the points of maximum reaction in the vibrating column of gas. Two oscillators, of approximate frequencies 94 and 450 kc respectively, were employed as before; their exact frequencies were read by analysis of a heterodyne note with a standard crystal on an impedance bridge, and were known to 0.05 percent. Displacements of the plane-ground Pyrex reflectors were measured to 0.005 mm by specially ground micrometer screws. The reflecting piston of the 94 kc apparatus could be moved 12 cm from the face of the oscillator, and that of the 450 kc apparatus to a distance of 5 cm; these large displacements were necessary to secure the requisite number of half-wave-length measurements for an accurate determination in a gas in which the velocity of sound is about 1400 m sec.$^{-1}$. Both micrometer screws were surrounded by housings which could be

[2] Richards and Reid, J. Chem. Phys. **1**, 114 (1933).
[3] Pierce, Proc. Am. Acad. **63**, 1 (1928).

evacuated independently of the inner acoustical chambers. A thorough evacuation of the apparatus was therefore always an easy matter. All measurements were made at 30.0° in an oil thermostat maintained constant to better than 0.1°. The pressure at which the measurements were made was 780 mm±10 mm; the effect of considerably greater variations in pressure could not have been detected.

B. Measurements at velocities of sound greater than 375 m sec.$^{-1}$

The first series of measurements undertaken were intended to extend our knowledge of the supposed "rotational dispersion of hydrogen" which had previously been reported[1] on the basis of measurements where the maximum displacement of the piston from the face of the oscillator was only 2.5 cm. Concerning the previous measurements it was stated "determinations at 94 kc which result in a velocity of sound greater than 400 m sec.$^{-1}$ are of considerably less accuracy than those below this figure. This is both because the tube-correction has not been determined for the apparatus at large velocities, and because the dimensions of the apparatus did not permit the detection of many points of maximum reaction when the wavelength was large." Nevertheless, since the velocity measured at 450 kc was much greater than that found by Cornish and Eastman,[4] since a tube-correction could only have lowered this if due to the causes discussed by Helmholtz and Kirchhoff,[5] and since the measurements agreed well with the expression derived from the assumption that both hydrogen and ethylene were dispersive, the increase in velocity of sound in hydrogen at 450 kc was believed to be real. Although conclusive evidence is at hand that this belief was fallacious no refutation of the first two of these arguments is at present available.

Measurements were undertaken on pure hydrogen and helium, and on hydrogen-helium, hydrogen-ethylene, hydrogen-argon, and helium-argon mixtures. Only a few of these were necessary to demonstrate that the interpretation of the previous work was seriously in error. The differences between the velocity of sound at 450

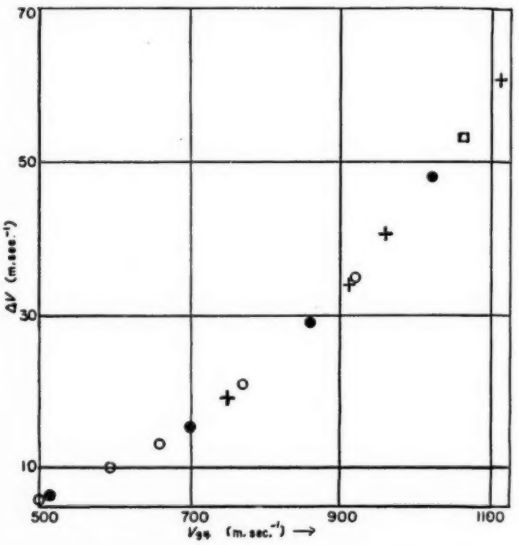

FIG. 1. $V_{451} - V_{94}$ (uncorrected) plotted as a function of V_{94} for nondispersive gases. Helium-argon mixtures are represented by open circles, hydrogen-argon by closed circles, hydrogen-ethylene by crosses, and hydrogen-helium by squares.

and 94 kc (which has been termed ΔV and made the axis of ordinates in Fig. 1) fell on a consistent and well-defined curve conditioned by the magnitude of the velocity alone, and quite independent of the composition of the mixture. Since it is contrary to all present theory to suppose that helium should be dispersive in this range of temperature, pressure, and frequency, and since, furthermore, it is highly unlikely that either helium or argon could be as effective as ethylene in exciting the rotational states of hydrogen, it became apparent that the results merely determined the tube or apparatus-correction for the pair of oscillators, and that the supposed dispersion of hydrogen was nonexistent. The measurements leading to this conclusion will not be published, since no especial care concerning either purity or composition was exercised. Fig. 1, which is a graphical representation of some of the results, establishes the fictitious character of the "rotational-dispersion" of hydrogen with sufficient clearness.

It must again be stressed that the increase of velocity in hydrogen at 450 kc over its value at low frequencies although purely an apparatus effect is yet to be explained. Errors in the measurement of length could not, conceivably, be great enough to explain it. Since the heterodyning

[4] Cornish and Eastman, J. Am. Chem. Soc. **50**, 1 (1928).
[5] See Cornish and Eastman, Phys. Rev. **33**, 90 (1929).

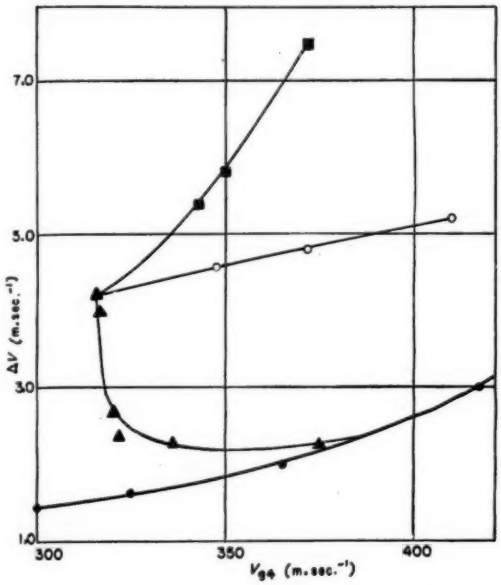

FIG. 2. Uncorrected measurements on ethylene-hydrogen mixtures (triangles) ethylene-helium mixtures (squares) ethylene-deuterium mixtures (open circles) and non-dispersive gases (black circles). The solid lines have been drawn merely as an aid to the eye, and do not result from calculations.

of a high harmonic of the standard crystal against the magnetostriction oscillator allows the possibility that the harmonic has been improperly identified, the oscillator was compared with two calibrated valve-tube oscillators, one of which was purchased commercially, and the other of which was made and calibrated to 0.1 percent by Mr. C. Butt. In both cases the frequency of the magnetostriction oscillators was confirmed.

Forunately the resulting error in attributing dispersion to hydrogen was soon corrected by other writers. Almost simultaneously and independently Roy and Rose[6] and Kneser and Wallmann[7] demonstrated by measurements that our interpretation was false, and the former included a most interesting theoretical justification of this demonstration.

C. Measurements on deuterium and deuterium-ethylene mixtures

In view of what has been found in the previous section both reader and investigator must pause to inquire whether measurements at velocities below 375 m sec.$^{-1}$ have significance. In answer to this question Fig. 2 is presented, in which the values of $V_{450}-V_{94}$ are plotted against the velocity at 94 kc ($=V_{94}$). The figures incorporated in this graph are wholly uncorrected for tube or apparatus effects, in contrast to the values published in earlier reports. It is apparent that, although there is an increasing apparatus-correction, the dispersive behavior of hydrogen-ethylene and of helium-ethylene mixtures is well defined and significant. The method of computation was such that none of the previous conclusions need be altered for cases where the tube-correction was known, that is where V_{94} $=375$ m sec.$^{-1}$. It should perhaps also be pointed out that most of the previous measurements reported from this laboratory were made with oscillators of 2.5 cm diameter at 9 and 92 kc, and have no possible connection with the peculiar effect found only with the 1 cm 451 kc oscillator.

Measurements on deuterium-ethylene mixtures were made with especially purified ethylene (rated 99.9 percent) and deuterium obtained by the electrolysis of the best "heavy water" made in this laboratory, and purified by passing over glowing platinum and diffusion through a palladium thimble. The velocity of sound in the pure ethylene at 451 kc was identical with that previously found in somewhat less pure samples. The deuterium used has since been found to contain 1 mole percent of hydrogen,[8] and allowance for this has been made in the calculations. The gaseous mixture was prepared in a glass cylinder of about 1 liter capacity which was sealed to the apparatus. This cylinder and the two acoustical chambers were simultaneously evacuated, and it was then isolated from them by a stopcock. A quantity of ethlyene was then admitted, and the cylinder sealed to the deuterium generator. The cylinder was then plunged into carbon-dioxide-acetone slush, and filled to atmospheric pressure at this temperature. It was finally reconnected with the acoustical system and warmed until the pressure in the apparatus attained 780 mm, when the acoustical system was sealed off. Considerable care was exercised to assure thorough mixing of the two components. It is now possible to state with some assurance that exchange reactions with hydrogen or water adsorbed on the glass

[6] Roy and Rose, Proc. Roy. Soc. **A149**, 511 (1935).
[7] Kneser and Wallmann, Naturwiss. **30**, 510 (1934).
[8] Dr. N. R. Trenner, private communication.

walls of the acoustical chambers, on stopcock grease, or on the nichrome oscillators, could not have altered the composition of the mixture.[9, 10] Additional evidence to this effect was found in the constancy of the velocity over periods of 24 hours.

In reporting the measurements the system of corrections previously used, which consisted merely of adding to the velocity at 94 kc the difference between V_{450} and V_{94} is a nondispersive mixture of identical velocity, must clearly be discarded, since it has been conclusively demonstrated that the 450 kc measurements are the chief cause of this difference. Instead, a small correction obtained by the Helmholtz-Kirchhoff formula,[5] was added to the velocity at 94 kc, and the "true" velocity at 450 kc found by subtracting from the measured velocity the apparatus correction discussed in Section B revised to include the Helmholtz-Kirchhoff effect. In this way values for ΔV were obtained which were as accurate as the reproducibility of the measurements, and absolute values of the velocities secured, which are in error by less than 0.5 percent. An absolute error several times this would not affect the conclusions here supported. The reproducibility of the measurements was about ± 0.01 percent, as usual. The velocities reported in Table I have been treated in this way. The velocity for "pure" deuterium is about 0.16 percent below that to be expected from this gas containing 1 mole percent of hydrogen, but a part, at least, of this difference is due to van der Waals forces, which have not been considered in the calculation.

It should perhaps be added that two sets of measurements in ethylene-propane mixtures were made. These indicated that propane behaved very much as an indifferent gas, being somewhat less effective than ethylene itself in exciting the ethylene vibrations. The values of the velocity obtained showed, however, poor agreement with calculated values, doubtless due to impurities in the propane. For this reason they will not be printed.

[9] Gould, Bleakney and Taylor, J. Chem. Phys. **2**, 362 (1934).

[10] Horiuchi and Polanyi, Nature **132**, 819 (1933); A. Farkas, Trans. Faraday Soc. **32**, 922 (1936).

Calculation

Since no chemical analysis of the binary gaseous mixture had been undertaken, it was necessary to ascertain its composition from the velocity at low frequency. The computation was made directly from the familiar equation

$$V_0^2 = RT/\overline{M}\{(\overline{C}+R)/\overline{C}\}, \qquad (1)$$

in which V_0 is the low frequency velocity, R the gas constant, $\overline{C}=C_A m+C_B(1-m)$ the A and B subscripts referring to the equilibrium heat capacity of ethylene and deuterium respectively, and m the mole fraction of ethylene. Although a recent discussion of the heat capacity of ethylene has appeared,[11] our knowledge of it has not been greatly advanced, and $C_A=8.20$ cal. mole^{-1} was used as before. The heat capacity of deuterium was taken as exactly $5/2R$ at all frequencies. The quantity $\overline{M}=28.37m+4.017(1-m)$ represents an adjusted average molecular weight for the mixture. Two types of adjustment were necessary: one the apparent increase of the molecular weight of both components to compensate for association due to van der Waals forces, and the other the decrease of the effective molecular weight of deuterium owing to the fact that it contained 1 mole percent of hydrogen. These adjustments have been carried out rigorously in keeping with the principles laid down in Part III of this series, and the resulting value for $\overline{M}$ is considered good at least to 0.1 percent. In this the figures defining the composition of the C_2H_4–D_2 mixtures, which are recorded in Table I, were secured.

The relaxation times characteristic of the various mixtures were then secured from the

Table I. *The velocity of sound in ethylene-deuterium mixtures at 780 mm and 30°.*

Mole Fraction of Ethylene	Velocity at 94 kc in m sec.$^{-1}$	Velocity at 451 kc in m sec.$^{-1}$	ΔV_{obs} m sec.$^{-1}$	ΔV_{calc} m sec.$^{-1}$
1.000	332.2	334.7	2.5	—
0.9036	348.2	350.9	2.7	2.6
.7854	371.2	373.8	2.6	2.6
.6294	409.1	411.4	2.3	2.4
.00	937	937	0	—

[11] Teller and Topley, J. Chem. Soc. 885 (1935). These writers were concerned with an analysis of the vibrational frequencies of ethylene, and frankly admit the inadequacy of the calorimetric data.

velocities at 450.7 kc by the equation

$$\vartheta = \frac{\bar{C}}{\bar{C}_\infty \omega}\left\{\frac{V_\omega^2 - V_0^2}{V_\infty^2 - V_0^2}\right\}^{\frac{1}{2}}, \qquad (2)$$

where ϑ is the relaxation time, $\bar{C}$ identical with the same quantity in (1), $\bar{C}_\infty = C_{\infty A}\cdot m + C_B(1-m)$, $\omega = 2\pi \cdot 4.507 \times 10^5$, and V_ω the measured velocity at 450.7 kc. V_0 is defined by (1) and V_∞ by a similar equation in which $\bar{C}_\infty$ is substituted for $\bar{C}$. The relative effectiveness per unit concentration of ethylene and deuterium, ϵ, then follows from the relation

$$\epsilon = (\vartheta_A - m\vartheta)/\vartheta(1-m), \qquad (3)$$

where ϑ_A is 2.6×10^{-7} sec., the characteristic time for pure ethylene at 30°C and 780 mm pressure. Thus it was found that the contaminated deuterium was 1.50 times as effective per unit concentration as ethylene. The contamination of hydrogen, whether in the form HD or H_2, would reduce this figure by some ten percent. Furthermore, from ordinary kinetic considerations it follows that an ethylene molecule suffers 1.14 times as many collisions in a given concentration of deuterium as in a similar concentration of ethylene. Hence *per collision* an encounter with a deuterium molecule is 1.27 times as effective as an encounter with an ethylene molecule in exciting the lower vibrational states of ethylene.

In order to assure comparability with the result previously reported that a hydrogen-ethylene collision was 10 times as effective as an ethylene-ethylene collision, the measurements previously reported for hydrogen-ethylene mixtures were recalculated using the revised system of corrections described in Section C of the experimental part. Fig. 3, which represents both the hydrogen and deuterium results graphically, shows that the factor 10 is unchanged by the revision, and that both calculated curves agree with experiment to better than 0.06 percent. That a revision of the corrections applied does not alter the result may appear surprising, but it is easily accounted for by the fact that characteristic times are always obtained by using the differences in measured values, as illustrated by (2) above. Such a procedure, which was deliberately adopted at the start of this series of acoustical studies when it became apparent that tube corrections might render somewhat uncertain the absolute velocities, makes even grave errors in absolute velocity unimportant. Hence it may be said with some confidence, on the basis of Fig. 3, that a hydrogen-ethylene collision is eight times as effective as a deuterium-ethylene collision.

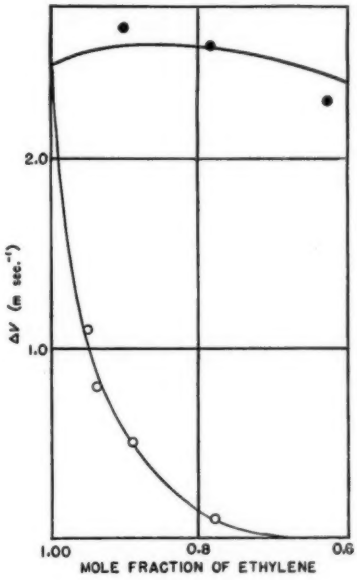

FIG. 3. $V_{451} - V_{94}$, corrected for apparatus effects, plotted as a function of composition for ethylene-hydrogen (open circles) and ethylene-deuterium (solid circles) mixtures. The solid lines have been computed on the assumption that an ethylene-hydrogen collision is ten times as effective as an ethylene-ethylene collision and eight times as effective as an ethylene-deuterium collision. The lower curve serves to correct Fig. 5 reference 1.

It is felt that the measurements are capable of providing an extra significant figure to this number, but that the uncertainties of calculation, chief among which are the variable hydrogen content of the deuterium used, and the possible incorrectness of the heat capacity of ethylene, do not warrant further laboring of the figures.

DISCUSSION

The decided difference which has been found between the effectiveness of hydrogen and deuterium in exciting the lower vibrational states of ethylene appears conclusively to eliminate any explanation for hydrogen's superiority which is based on mass alone. Excitation by a classical

impact, as suggested by Oldenberg,[12] should yield an effectiveness over deuterium which is less than two. Similarly an explanation, like that of Franck and Eucken,[13] which regards the excitation of the lower vibrational states as a prelude to chemical reaction, and consequently predicts parallel behavior for both hydrogen and deuterium, cannot be considered. Here again, since the eigenfunctions of the two molecules are practically identical, the only observable difference should be the mass factor appearing in the collision rate.

There remain two general possibilities. The first of these is concerned with the uniquely small moment of inertia of hydrogen. It appears at least possible that the magnitude of the rotational quanta which are exchanged with the ethylene molecule may be connected with the conspicuous effectiveness of hydrogen in exciting vibrational energy. If approximate "matching" or resonance occurred between a hydrocarbon vibrational quantum and a group of hydrogen rotational quanta the effect would be explained, since the distribution of rotational states of deuterium is quite different from that in hydrogen. After a preliminary survey of the computations necessary for the solution of this problem, the present writer has decided to leave it to others. Not only is its generalized formulation exceedingly difficult, but it is believed that the present knowledge of the vibrational frequencies of ethylene is insufficient to bring it to a successful conclusion. Alternatively, it is possible that the shortness of the duration of the collision of hydrogen with ethylene, in comparison with that of deuterium under similar circumstances, may provide an explanation. According to the treatment of Zener,[14] the mass here enters exponentially. Again, however, the problem becomes difficult, since the relation between the duration of the collision and the rate of transmission of the effect of the collision appears to be the determining factor. An instantaneous blow on one of the hydrogens in ethylene would provoke severe distortional vibrations of the molecule, whereas if it were struck sufficiently slowly the result would be merely to make the molecule rotate as a whole. It must therefore be left undecided whether either of these two mechanisms is capable of providing an acceptable quantitative description of the measurements.

This investigation was originally undertaken with a view to comparing the collision efficiencies of hydrogen and deuterium found by acoustical measurements with those found from chemical reaction rates. It is somewhat ironical, therefore, that no trustworthy data for chemical reactions appear to be at present available.

[12] Oldenberg, Phys. Rev. **37**, 194 (1931); Heil, Zeits. f. Physik **14**, 31 (1932).
[13] Franck and Eucken, Zeits. f. physik. Chemie **B20**, 460 (1933).
[14] Zener, Phys. Rev. **38**, 277, 556 (1931).

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Acoustical Studies

VI. Observations Concerning the Behavior of Formic and Acetic Acid Vapors

C. O. STROTHER AND W. T. RICHARDS, *Princeton University*
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The thermal decomposition of formic acid at 60°, the lowest temperature at which its vapor pressure is great enough to permit the determination of the velocity of sound, was sufficiently rapid to make accurate measurements impossible. Measurements on acetic acid vapor at several temperatures are reported which serve to place the lower limit of the dissociation rate at about 10^4 sec.$^{-1}$ at 85° and 174 mm. Reasons for the variability of the velocity of sound in acetic acid, which is in sharp contrast with the behavior of nitrogen tetroxide, are discussed.

Introduction

THE success of the acoustical method in determining the dissociation rate of nitrogen tetroxide suggests its application to other rapidly dissociating gases. Among these formic and acetic acids appear especially suitable since their dissociation heats are large, and since they attain sufficient vapor pressures to permit acoustical measurements below 100°. This communication reports exploratory observations on both substances. Since the success attained was meager the report will be brief, but it is believed that the measurements were carried out with sufficient care to warrant their publication as a warning to others who may wish to undertake the same task.

Apparatus and Purification of Materials

The apparatus employed was essentially that already described by Richards and Reid.[1] It was, however, modified in several respects to make high temperature measurements possible. The bulb containing liquid which provided pressure regulation in the acoustical chamber (*F* of Fig. 3[1]) was thermostated by a vapor bath with automatic pressure control.[2] In this way the liquid was kept at constant temperature ±0.01°, and pressure regulation considerably better than that required for 0.1 percent accuracy of the velocity of sound secured in the acoustical chamber. All tubing not in the vapor bath, or in the thermostat which surrounded the acoustical chamber, was wound with calibrated chromel wire, and kept about 20° above the temperature of the acoustical chamber. The main thermostat was filled with transformer oil and controlled by a mercury regulator to ±0.1°. The necessity for preventing condensation in the tubing made the use of a quartz manometer inconvenient, and in its place a mercury manometer was employed. In this way a rough check on the vapor pressures given in the literature for formic and acetic acids was obtained. In the case of the former substance a manometer proved especially valuable since it gave an indication of the rate of decomposition. The oscillators were the same as those used for nitrogen tetroxide, but were driven by an "electron coupled" circuit which gave greater stability and more uniform deflections at the points of maximum reaction than the oscillator previously employed.

The method of measurement was essentially that already described: the liquid was distilled into the apparatus in vacuum, frozen, and the apparatus thoroughly exhausted by a good oil pump. The acoustical chamber was then flushed many times with vapor before measurements were undertaken. Whenever possible measurements at high and at low frequency were made on the same day on the same sample of vapor. Small tube corrections, obtained as described previously, have been applied when necessary to all the values which are quoted below.

A trial with normal heptane, which was used to calibrate the apparatus, served to demonstrate that between 85° and 106° measurements reproducible to ±0.05 percent were easily obtainable. The variability of the results recorded below is not, therefore, due to any defect in the details of measurement.

The formic acid was the commercial C. P. grade. Two samples of acetic acid were employed. Both were obtained by purification of the pure commercial acid (rated 99.5 percent). Sample I was recrystallized seven times, introduced quickly into the apparatus to prevent the accumulation of moisture, and distilled in vacuum three times. Sample II was recrystallized eight times, the melting point remaining constant after the first two crystallizations. It was then twice recrystallized in vacuum, introduced into the apparatus by the use of a "magnetic break," and three times distilled in vacuum before measurement. The melting point of both samples was 16.8°.

Formic Acid

Formic acid is thermodynamically unstable at ordinary temperatures, and even in glass vessels an appreciable amount of thermal decomposition of the liquid may be observed at room temperature.[3] At temperatures of 60° and above the decomposition is sufficiently rapid to require consideration even when the vapor density is being determined. Each determination of the velocity of sound requires about three hours with a gas of constant composition, and the rate of decomposi-

[1] Richards and Reid, J. Chem. Phys. **1**, 120 (1933), Fig. 3.
[2] Kuentzel, J. Am. Chem. Soc. **51**, 3347 (1929).
[3] Coolidge, J. Am. Chem. Soc. **50**, 2166 (1928).

tion, doubtless increased by the presence in the system of the extensive nickel and nichrome surfaces of the oscillators, proved an insuperable obstacle to accurate determinations. No measurements on formic acid are reported for this reason. The development of an acoustical method which permits rapid determinations suggests itself as the only means of overcoming this difficulty.

Acetic Acid

The measurements on acetic acid have been summarized in Table I, which is self-explanatory. The pressures at which the measurements were made were determined from the temperature of the vapor bath and interpolation of the values for the vapor pressure of acetic acid quoted in the *International Critical Tables*. Unfortunately the measurements show variations which are larger by one order of magnitude than the experimental error. Since the variations follow, however, a relatively consistent course with time and with method of treatment, a systematic explanation suggests itself. The velocity of sound systematically increased the greater the "purity" of the sample, i.e., the larger the number of times it had been pumped out or recrystallized. Since the reverse is to be expected with a heavy vapor such as acetic acid, it appears possible that the inclusion of water in the form of a coordination compound $HAc \cdot H_2O$, similar in structure to that suggested by Sidgwick[4] for $(HAc)_2$, may here be the determining cause. The very diverse values of the density, vapor pressure, and the like encountered in the literature suggest difficulties in purification greater than those to be encountered in a mere mixture of two molecular species. If this is the case pure acetic acid, either in liquid or vapor, would be difficult indeed to obtain.

The data with which to compare these velocities are meager and sadly confused; this is perhaps the most potent reason for publishing them. The only measurement on the velocity of sound is due to Stevens[5] and cannot serve as a basis of comparison since it is at 136° and 760 mm. The most recent study of the vapor density and heat of dissociation of acetic acid is that of Fenton and Garner,[6] who found the heat of dissociation to be 13,790 cal. mole^{-1} at constant volume, a value somewhat higher than that reported by Ramsey and Young.[7] From the figures of Fenton and Garner and the expression of Einstein[8] for the velocity of sound in an ideal dissociating gas there result the values of 202, 193, and 186 meters sec.$^{-1}$ for the velocity of sound at low frequency and 115°, 402 mm; 95°, 174 mm; and 85°, 174 mm, respectively. These are consistently above the measured values, as Table I shows. The discrepancy cannot be attributed to neglect of the van der Waals forces, since the calculation employs the measured vapor densities, and the approximation that the gas is ideal enters only into the insensitive compressibility ratio.[9] The older data of Young[10] for the saturation densities of acetic acid are about six percent higher than those extrapolated from Fenton and Garner in the temperature range which here comes into consideration. If they are interpolated over a small pressure range by means of the ideal gas laws they give a much better agreement with experiment than is provided by the data of Fenton and Garner. This procedure is, however, not wholly defensible.

Table I. *The velocity of sound in acetic acid vapor at various temperatures, frequencies, and pressures.*

Linear Frequency (kc)	Measured Velocity of Sound (m sec.$^{-1}$)	Calculated Velocity of Sound (m sec.$^{-1}$)
	Sample I	
	85.0±0.1° and 174 mm	
9.242	182.1[a]	185.8
91.26	182.3[a]	——
	95.0±0.1° and 174 mm	
9.212	190.7	193.1
91.21	190.7	——
	110.0±0.15° and 403 mm	
9.246	189.5	——
	115 ±0.15° and 403 mm	
9.218	194.0	201.9
90.80	194.3	——
	Sample II	
	84.9±0.1° and 174 mm	
9.242	183.4[b]	185.7
91.26	183.8[b]	——
	95.6±0.1° and 174 mm	
9.209	193.5	193.1
91.18	193.3	——

[a] The average of two independent determinations.
[b] The average of four independent determinations.

[4] Sidgwick, Chem. Soc. Ann. Reports **30**, 115 (1933).
[5] Stevens, Ann. d. Physik **7**, 320 (1907).
[6] Fenton and Garner, J. Chem. Soc., 694 (1930).
[7] Ramsey and Young, J. Chem. Soc. **49**, 790 (1886).
[8] Einstein, Sitz, Ber. Akad., 380 (1920).
[9] For a discussion of this see Richards and Reid, J. Phys. Chem. **1**, 747 (1933).
[10] Young 1910, quoted in Landholdt and Bornstein.

In view of this confusion an attempt was made to establish the vapor density and heat of dissociation by means of the acoustical measurements alone. For this purpose the velocity of sound at low frequency in a dissociating gas is written, after Einstein[8]

$$V_0^2=\frac{RT(1+\alpha)}{M_2}\times\left\{\frac{R(B+1)^2(\alpha-\alpha^2)+2(\bar{C}_0+R)}{(RB^2+\bar{C}_0)(\alpha-\alpha^2)+2\bar{C}_0}\right\}, \quad (1)$$

where V_0 is the phase velocity of sound at low frequency, R the molecular gas constant, T the absolute temperature, α the degree of dissociation, M_2 the molecular weight of the heavy molecule, $\bar{C}_0$ the average heat capacity of double and single molecules at low frequency, and B an abbreviation for D/RT where D is the heat of dissociation at constant volume. The neglect of the van der Waals corrections in this expression is no more grave than the similar approximation usually made in obtaining the dissociation heat as, for example, in the work of Fenton and Garner.[6] Eq. (1), although cubic in α, permits the determination of $\alpha=f(P, T)$ by successive approximation because of the fact that the quantity in brackets is, with a gas of large dissociation heat and heat capacity, almost independent of temperature and very near to unity. Unfortunately the quantities for D so obtained, although centering about 14,000 cal. mole^{-1}, varied from 16,000 to 10,000 depending upon which pair of determinations was chosen for the calculation. The situation must therefore be abandoned as hopeless.

A few words should be said concerning the heat capacities employed in the calculations described above. Since there are, of course, no experimental determinations of these quantities, they must be deduced. By summing the energies of Planck-Einstein oscillators, with frequencies obtained largely from Raman spectra, values for the heat capacities of the single and double molecules were obtained which, it is believed, were not seriously in error from the standpoint of the present study. The model for the single molecule gave 12.0, 11.5, and 11.3 cal. mole^{-1} at 115, 95 and 85°; that for the double molecule 16.5, 15.7, and 15.4 cal. mole^{-1} at the same temperatures. These were used consistently in calculations concerning the low frequency velocity.

It remains only to set a lower limit for the rate of dissociation of $(HAc)_2$. Here the conditions are, of course, far less favorable than those obtaining in nitrogen tetroxide owing to the relatively large heat capacity of acetic acid. A change from the low frequency velocity, where the dissociation reaction is in equilibrium with the acoustical cycle, to the high frequency velocity where the dissociation reaction wholly fails to participate in the compressibility ratio, would mean a change of only some two to three meters sec.$^{-1}$ in the velocity of sound under the conditions here reported. As a consequence it is extremely difficult, in acetic acid, to identify the cause for any dispersion which may be found; if a part of the heat capacity fails to follow the acoustical cycle it may cause a change in the compressibility ratio comparable to a failure of the dissociation reaction. This is in sharp contrast to the conditions in nitrogen tetroxide. It is, in fact, a serious limitation of the acoustical method of determining reaction rates that it can effectively be employed only with gases of relatively low heat capacity and high dissociation heat. However, since at 85° and 174 mm no dispersion has become clearly manifest at 91 kcal., it is reasonable to attribute a minimum reaction rate of 10^4 sec.$^{-1}$ to the dissociation of $(HAc)_2$ under these conditions. It is hoped that this figure, at least, may prove of interest.

We are indebted to Mr. Alfred L. Loomis for funds which permitted the junior author to undertake this investigation.

The Radiochemical Synthesis and Decomposition of Hydrogen Bromide

H. EYRING, J. O. HIRSCHFELDER AND H. S. TAYLOR, *Frick Chemical Laboratory, Princeton University*

(Received June 24, 1936)

A theory is developed for the radiochemical synthesis and decomposition of hydrogen bromide which makes use of experimentally known processes of ionization, the known rates of a few simple chemical reactions, and the extensive experimental results of Lind and Livingston. The analysis indicates that in pure hydrogen gas, six hydrogen atoms are formed per ion pair; in pure hydrogen bromide, six hydrogen bromide molecules would be decomposed; and in equal mixtures of Br_2 and HBr the chance that an electron will form negative ions with HBr ($HBr+\epsilon \rightarrow H+Br^-$) is greater than with Br_2.

IN most radiochemical experiments, the number of molecules reacting for each ion pair formed is largely independent of the stoichiometrical composition of the mixture of gases. However, the recent very careful investigations of Lind and Livingston[1] show that the synthesis and decomposition of hydrogen bromide vary greatly with the relative pressures of the hydrogen, bromine and hydrogen bromide. In this paper, we develop an explanation for the observed yields which is based upon a knowledge of the processes of ionization in these gases and the rates of a few simple chemical reactions.

1. *The Primary Ionization Processes.*—The ionization processes in pure hydrogen have been considered in a previous paper.[2] The alpha-particle ionizes the hydrogen to form H_2^+.

$$H_2+\alpha \rightarrow H_2^+ + \epsilon + \alpha. \quad (1)$$

The formation of H^+ is less frequent. There is considerable evidence that the alpha-particle gives up part of its energy by exciting the molecules without ionizing them.

$$H_2+\alpha \rightarrow H_2' + \alpha. \quad (2)$$

These energy rich molecules may subsequently dissociate to form two hydrogen atoms. The energy of the alpha-particle consumed is equivalent to 33 ev per pair of ions produced. Since the ionization process requires 15.4 ev per ion pair as minimum ionization energy it is evident that quantities of energy roughly equivalent to those consumed in ionization may be used for molecular excitation.

Blewett[3] has recently studied in the mass spectrograph the ionization processes in bromine for slow electron collisions. He finds that Br_2^+ and Br^+ are formed. For the high speed collisions between alpha-particles and bromine molecules it is impossible at present to say on the basis of experiments alone which ionization would occur most frequently. Also, bromine atoms will be formed by the intermediate production of excited bromine molecules. However, it is quite immaterial for the purposes of this paper to consider these species since we shall find that the bromine atoms as well as the bromine positive ions cannot essentially affect either the synthesis or the dissociation of hydrogen bromide.

Little work has been done with the mass spectrograph on the ionization processes in hydrogen bromide. However, Blewett obtained HBr^+ from impurities in his bromine gas and this is undoubtedly the principal ion which is first formed in the hydrogen bromide. Just as in the case of hydrogen and of bromine, we should also expect the formation of excited molecules which subsequently dissociate to form the separate atoms.

$$HBr+\alpha \rightarrow HBr' \rightarrow H+Br. \quad (3)$$

The yield of H_2+Br_2 from HBr per ion pair, which Lind and Livingston measured, provide excellent data for determining the frequency with which reactions of type (3) occur.

2. *Secondary Ionization Processes in the Individual Gases.*—There is considerable evidence that the reaction:

$$H_2^+ + H_2 \rightarrow H_3^+ + H \quad (4)$$

[1] Lind and Livingston, J. Am. Chem. Soc. **58**, 612 (1936).
[2] Eyring, Hirschfelder and Taylor, J. Chem. Phys. **4**, 479 (1936).
[3] Blewett, Phys. Rev. **49**, 900 (1936); Blewett, Ph.D. dissertation, Princeton, 1936.

takes place with great frequency.[2] The corresponding reactions for bromine ions:

$$\begin{aligned} Br_2^+ + Br_2 &\rightarrow Br_3^+ + Br \\ Br^+ + Br_2 &\rightarrow Br_3^+ \end{aligned} \qquad (5)$$

have not been investigated, but their occurrence is immaterial from the standpoint of this paper. With hydrogen bromide this type of reaction is of considerable interest:

$$HBr^+ + HBr \rightarrow H_2 + Br_2^+ \qquad (6a)$$

$$\rightarrow H_2Br^+ + Br. \qquad (6b)$$

Reaction (6a) requires an energy of 7 kcal. if we consider the following thermal data:

$$\begin{aligned} Br_2 &\rightarrow Br_2^+ + \epsilon - 12.8 \text{ ev} \\ HBr^+ + \epsilon &\rightarrow HBr + 13.2 \text{ ev} \\ 2HBr &\rightarrow H_2 + Br_2 - 16 \text{ kcal.} \end{aligned}$$

This value for the necessary energy is within the estimated limits of error of the ionization potentials of HBr and of Br_2, i.e., 0.5 ev, and might therefore be spurious. Blewett has observed the presence of H_2Br^+ ions, and reaction (6b) can occur if the binding of H_2 to Br^+ exceeds 30 kcal. since:

$$\begin{aligned} HBr^+ + \epsilon &\rightarrow HBr + 13.2 \text{ ev} \\ 2HBr &\rightarrow H_2 + Br_2 - 16 \text{ kcal.} \\ Br_2 &\rightarrow 2Br - 46 \text{ kcal.} \\ Br &\rightarrow Br^+ + \epsilon - 11.8 \text{ ev} \\ \hline HBr^+ + HBr &\rightarrow H_2 + Br^+ + Br - 30 \text{ kcal.} \end{aligned}$$

This required binding energy of Br^+ with H_2 of more than 30 kcal. does not seem excessive since we know that Br^+ binds H to form HBr^+ with 50 kcal. and also that H^+ binds H_2 with more than 50 and probably 70 kcal. Lacking further information we shall, therefore, consider reaction (6b) as occurring frequently and rule out reaction (6a) from energy considerations.

The fate of electrons in H_2, Br_2, and HBr is well known. The electron affinity of H is so small and the activation energy required for its formation so great that

$$H_2 + \epsilon \rightarrow H + H^-$$

is indeed a rare process. However, bromine has such a large electron affinity,[3,4] i.e., 88 kcal., that slow electrons are rapidly absorbed in HBr and Br_2 to form Br^- ions. Some Br_2^- ions are also formed. It is interesting to note that Blewett was unable to detect any HBr^- ions. In the interpretation of the synthesis and decomposition of hydrogen bromide we will have to consider the relative rate of reaction of an electron with HBr and with Br_2. The negative ions formed neutralize the positive ions liberating free atoms, etc. As we shall show later, our conclusions from the Lind and Livingston experiments indicate that an electron in a mixture of equal amounts of HBr and Br_2 reacts more often with HBr than with Br_2.

Combining the various processes, we obtain for the mechanisms in the pure gases:

(a) Hydrogen:

$$\begin{aligned} H_2 + \alpha &\rightarrow H_2^+ + \alpha + \epsilon \\ H_2 + \alpha &\rightarrow H_2' + \alpha \rightarrow 2H + \alpha \\ H_2^+ + H_2 &\rightarrow H_3^+ + H \\ H_3^+ + \text{electron or negative ion} &\rightarrow \begin{matrix} H + H_2' \\ \text{or} \\ 3H \end{matrix} . \end{aligned}$$

The yield of H atoms per ion pair is therefore approximately 4 for those molecules which are dissociated by the ionic mechanism. To these must be added whatever H atoms are produced by dissociation without ionization. Our interpretation of the Lind and Livingston experiments indicate that 2 H atoms are produced per ion pair in this latter fashion. This yield is in agreement with our interpretation of the *ortho-para* hydrogen conversion which was studied by Capron.[5]

(b) Bromine: For our purposes the yield of Br atoms from Br_2 molecules is quite immaterial. The principal reactions probably are:

$$\begin{aligned} Br_2 + \alpha &\rightarrow Br_2^+ + \epsilon + \alpha \\ &\rightarrow Br^+ + Br + \epsilon + \alpha \\ Br^+ + Br_2 &\rightarrow Br_3^+ \\ Br_2^+ + Br_2 &\rightarrow Br_3^+ + Br \\ \epsilon + Br_2 &\rightarrow Br + Br^- \\ Br^- + Br_3^+ &\rightarrow 4Br. \end{aligned}$$

This would indicate that around 6 Br atoms are formed in the ionic processes per ion pair and to this must be added the number which are formed by dissociation of Br_2 without ionization.

(c) Hydrogen Bromide:

[4] Glockler, A. C. S. Meeting, Kansas City, 1936

[5] Capron, Ann. soc. sci. Bruxelles **B55**, 222–36 (1935).

$$HBr+\alpha\rightarrow HBr^{+}+\epsilon+\alpha$$
$$HBr^{+}+HBr\rightarrow H_2Br^{+}+Br$$
$$HBr+\epsilon\rightarrow H+Br^{-}$$
$$Br^{-}+H_2Br^{+}\rightarrow 2H+2Br$$
$$Br^{-}+HBr^{+}\rightarrow H+2Br.$$

Thus, between two and three H atoms are produced per ion pair through the ionic mechanisms.

3. *Secondary Ionization Processes in Mixed Gases.*—In addition to the ionic mechanisms which we have just considered, we must also examine the possibility of reactions in which the initial ionization in one gas produces effects in molecules of another species. H_2^+ can participate in two reactions of this nature.

$$H_2^{+}+Br_2\rightarrow HBr^{+}+HBr+67\text{ kcal.} \quad (7)$$
$$\rightarrow H+Br^{+}+HBr+17\text{ kcal.} \quad (7a)$$
$$H_2^{+}+HBr\rightarrow H_3^{+}+Br+26\text{ kcal.} \quad (8)$$
$$H_2^{+}+HBr\rightarrow H_2+HBr^{+}+51\text{ kcal.} \quad (8a)$$

Reactions (7) and (7a) cut down by one the yield of hydrogen bromide molecules in the synthesis since they are in competition with the reaction $H_2^{+}+H_2\rightarrow H_3^{+}+H$. The fact that we do not need to consider any such inhibitory property of Br_2 in our subsequent explanation of the synthesis indicates that (7) is not important, and suggests that the reaction may have a considerable activation energy. Reaction (8) may or may not occur but it does not affect the yield. Reaction (8a) would cut down the yield of H atoms and total yields in both synthesis and decomposition of hydrogen bromide.

Bromine ions could participate in the following:

$$Br_2^{+}+H_2\rightarrow HBr^{+}+HBr+7\text{ kcal.} \quad (9)$$
$$\rightarrow H_2Br^{+}+Br$$
$$Br^{+}+H_2\rightarrow H_2Br^{+}. \quad (10)$$

These would indicate that bromine should increase the yield over the values which we would expect from neglecting them. Either reaction (7) and either (9) or (10) occur and nicely counterbalance one another or else none of them occur with any frequency for the data on the synthesis of hydrogen bromide can be well explained for all ratios of H_2 to Br_2 neglecting such processes. It is interesting to note that the reactions:

$$Br_2^{+}+HBr\rightarrow Br_2+HBr^{+}-9\text{ kcal.} \quad (11)$$
$$Br^{+}+HBr\rightarrow Br+HBr^{+}-32\text{ kcal.} \quad (12)$$

are energetically improbable.

The HBr ions might react in the following manner:

$$HBr^{+}+Br_2\rightarrow Br_2^{+}+HBr+9\text{ kcal.} \quad (13)$$

Reaction (13) certainly is not important since we find a somewhat larger yield for the decomposition of HBr in the presence of Br_2 than we expect. The reaction

$$HBr^{+}+H_2\rightarrow H_3^{+}+Br-25\text{ kcal.} \quad (14)$$

is energetically improbable.

We may now analyze the data of Lind and Livingston first neglecting the effects of these ionic reactions between different species and then examining how far effects of these various types may influence the calculated yields.

4. *Synthesis and Decomposition of Hydrogen Bromide.*—In a mixture of hydrogen bromide, bromine and hydrogen the number of ion pairs found initially depends on the partial pressures, stopping powers, and specific ionizations of the gases present. The ratio of the number of positive ions of a species to the total number obeys a simple law of mixing:[6]

$$\frac{N_{H_2}}{N}=\frac{S_{H_2}I_{H_2}P_{H_2}}{S_{H_2}I_{H_2}P_{H_2}+S_{Br_2}I_{Br_2}P_{Br_2}+S_{HBr}I_{HBr}P_{HBr}},$$
$$\frac{N_{HBr}}{N}=\frac{S_{HBr}I_{HBr}P_{HBr}}{S_{HBr}I_{HBr}P_{HBr}+S_{H_2}I_{H_2}P_{H_2}+S_{Br_2}I_{Br_2}P_{Br_2}},$$
$$N=N_{HBr}+N_{H_2}+N_{Br_2}.$$

Here N with the appropriate subscript represents the number of ion pairs formed in the indicated gas. N without the subscript is the total number of ion pairs. The S's are the specific stopping powers of the gases and the I's are the specific numbers of ion pairs formed in the pure gases with respect to air = 1. The P's are the partial pressures of the gases and we shall express them in millimeters of mercury. The values of the stopping powers are well known and they should be quite accurate:[6]

$$S_{H_2}=0.24\quad S_{Br_2}=2.80\quad S_{HBr}=\tfrac{1}{2}(S_{H_2}+S_{Br_2})=1.52.$$

The values for the specific number of ion pairs are much more difficult to measure. The values which we use are:

$I_{H_2}=1.0$ (reference 6) $\quad I_{Br_2}=1.35$ (reference 6)
$I_{HBr}=1.29$ (reference 7)

[6] Glockler and Livingston, J. Phys. Chem. **38**, 655 (1934).
[7] Lind, "Chemical Effects of Alpha Particles," Chem. Monograph, p. 36 (1928).

and they may be inaccurate. Any error in these values will make corresponding errors in the following analysis. For example, if I_{HBr} were 1 instead of 1.29 we would find a yield of 5 instead of 6 H atoms per ion pair in nearly pure hydrogen containing small amounts of bromine.

After the ionic reactions have taken place a certain number of H and Br atoms are produced and also a certain number of hydrogen bromide molecules are formed or decomposed according to whether the initial ionization (or dissociation without ionization) has taken place in hydrogen, bromine or hydrogen bromide. The chemical reactions which these atoms may undergo have been carefully studied by Bodenstein, Lind, Jung, Bonhoeffer, and others.[8] Hydrogen atoms may react with either hydrogen bromide or with bromine:

$$H+Br_2 \xrightarrow{k_3} HBr+Br+36 \text{ kcal.}$$

$$H+HBr \xrightarrow{k_4} H_2+Br+16.7 \text{ kcal.}$$

In fact Bodenstein and Jung[9] have obtained an accurate value for the ratio

$$k_3/k_4=8.4.$$

Using this ratio, if B is the chance that an H atom will react with Br_2 to form HBr rather than reacting with HBr to destroy an HBr, then

$$B=\frac{k_3(H)(Br_2)}{k_4(H)(HBr)+k_3(H)(Br_2)}=\frac{1}{1+(1/8.4)(P_{HBr}/P_{Br_2})}.$$

The reactions of Br with HBr and with H_2 require too large an amount of energy to take place to any appreciable extent.

$$Br+HBr \rightarrow Br_2+H-36 \text{ kcal.} \quad (15)$$

$$Br+H_2 \rightarrow HBr+H-16.7 \text{ kcal.} \quad (16)$$

Before setting up an expression for the yield we must consider the probability that an electron will react with HBr to form Br^- rather than with Br_2 to form this same negative ion.

$$\epsilon+Br_2 \xrightarrow{k_1} Br^-+Br \quad (17)$$

$$\epsilon+HBr \xrightarrow{k_2} Br^-+H \quad (18)$$

We define the probability A of (18) occurring rather than (17) by:

$$A=\frac{k_2(HBr)}{k_1(Br_2)+k_2(HBr)}=\frac{1}{1+(k_1/k_2)(P_{Br_2}/P_{HBr})}.$$

The ratio of k_1/k_2 is not known experimentally but our interpretation of the Lind and Livingston data indicate that k_2 is considerably larger than k_1. The fact that the heat of dissociation of HBr, i.e., 82 kcal. is so close to the electron affinity of Br, 88 kcal., makes this seem plausible.

In the mixture of hydrogen, hydrogen bromide and bromine when the initial energy is taken up from the alpha-particle by hydrogen, let "a" H atoms be produced by going through positive ion reactions and subsequent neutralization and by dissociation without ionization. When this initial energy is taken up by hydrogen bromide, let "b" atoms of H be produced and "b" atoms of hydrogen bromide be thereby decomposed. The bromine, of course, produces no such effect owing to the nonreactivity of bromine with either hydrogen or hydrogen bromide. In each of these types of initial ionization, one electron is produced and is absorbed rapidly by either bromine or hydrogen bromide. This electron has the chance A that it will react with hydrogen bromide to produce an additional H atom and thereby decompose one more hydrogen bromide than if the electron were captured by bromine. Thus, altogether, the number of H atoms produced is:

$$aN_{H_2}+bN_{HBr}+AN.$$

The number of HBr molecules decomposed directly is:

$$bN_{HBr}+AN.$$

Remembering that each H atom has the chance B to react with Br_2 to form an HBr and a chance $(1-B)$ to decompose an HBr, we obtain for the yield of HBr per ion pair:

$$\frac{M}{N}=[B-(1-B)]\left[a\frac{N_{H_2}}{N}+b\frac{N_{HBr}}{N}+A\right]-b\frac{N_{HBr}}{N}-A$$

$$=a(2B-1)\frac{N_{H_2}}{N}-2b(1-B)\frac{N_{HBr}}{N}-2A(1-B).$$

[8] Morris and Pease, J. Chem. Phys. **3**, 796 (1935).
[9] Bodenstein and Jung, Zeits. f. physik. Chemie **121**, 127 (1926).

TABLE I. *Synthesis.*

Time, hrs.	P_{HBr}	P_{Br_2}	P_{H_2}	$(1-B)$	$(2B-1)N_{H_2}/N$	$(1-B)N_{HBr}/N$	$(M/N)_{calc.}$	$(M/N)_{obs.}$
10	3.0	120.5	167.5	.0030	.080	.000	.48	.58
30	8.4	117.8	164.8	.0084	.078	.000	.47	.58
50	12.8	115.6	162.6	.0130	.076	.001	.46	.54
70	16.2	113.9	160.9	.0167	.075	.001	.45	.48
90	18.8	112.6	159.6	.0195	.074	.001	.44	.43
110	21.0	111.5	158.5	.0219	.073	.002	.44	.44
130	23.0	110.5	157.5	.0242	.072	.002	.43	.45
150	24.6	109.7	156.7	.0260	.071	.003	.43	.47

TABLE II. *Decomposition (Assume $A=1$).*

Time, hrs.	P_{HBr}	P_{Br_2}	P_{H_2}	$(1-B)$	$(2B-1)N_{H_2}/N$	$(1-B)N_{HBr}/N$	$(M/N)_{calc.}$	$(M/N)_{obs.}$
10	148.3	10.6	10.6	.625	−.002	.545	−3.43	−3.57
30	127.9	20.8	20.8	.423	.002	.317	−2.13	−1.89
50	115.9	26.8	26.8	.340	.006	.231	−1.56	−1.51
70	107.3	31.1	31.1	.291	.009	.183	−1.25	−1.26
90	101.1	34.2	34.2	.260	.012	.154	−1.07	−1.08
110	96.3	36.6	36.6	.239	.014	.134	−.94	−1.01
130	92.7	38.4	38.4	.223	.015	.121	−.84	−.88
150	89.9	39.8	39.8	.212	.016	.111	−.76	−.82
170	87.7	40.9	40.9	.203	.017	.104	−.73	−.75

TABLE III. *Summary of experiments.*

Exp.	P_{HBr}	P_{Br_2}	P_{H_2}	$(1-B)$	$(2B-1)N_{H_2}/N$	$(1-B)N_{HBr}/N$	$(M/N)_{calc.}$	$(M/N)_{obs.}$
1	1.2	127.8	84.9	.0011	.040	.000	.24	.24
2	.6	115.4	126.2	.0006	.065	.000	.39	.42
3	3.0	120.5	167.5	.0030	.080	.000	.48	.58
4	2.4	95.5	250.4	.0030	.140	.000	.84	.88
5	5.4	56.6	411.3	.0112	.299	.000	1.79	1.90
6	2.4	58.4	469.3	.0049	.330	.000	1.98	1.76
7	7.8	40.0	456.1	.0227	.379	.001	2.27	2.67
8	3.8	26.4	424.6	.0169	.471	.001	2.83	2.76
9	3.4	29.7	515.1	.0135	.496	.000	2.98	2.85
10	6.4	25.1	502.2	.0295	.498	.002	2.99	2.85
11	4.6	17.9	510.3	.0297	.578	.001	3.47	2.89
12	71.9	136.1	1.0	.0592	.000	.013	−.17	−.89
13	162.3	4.5	4.5	.811	−.002	.768	−4.70	−3.98
14	148.3	10.6	10.6	.625	−.002	.545	−3.44	−3.57
15	105.7	5.5	579.5	.696	−.148	.393	−3.85	−2.57
16	84.5	1.3	571.1	.885	−.343	.477	−5.74	−5.07

Here B, N_{H_2}/N and N_{HBr}/N are known for any experiment. a, b, and a constant in A are not known and must be chosen so as to give the best fit with the experimental data. There are certain limits which we can place on these quantities *a priori*, i.e., $a>3$, $b>1$, and A lies between 1 and zero. We find the best agreement with experiment by taking

$a=6.0$, $b=2.0$, $A=1$ for large ratios of P_{HBr}/P_{Br_2}.

For smaller ratios the value of A is not important since $(1-B)$ is then small.

Tables I, II and III show the agreement which we obtain with the experiments of Lind and Livingston.[10] We must examine these tables for trends which would indicate the existence of important mixed ionic reactions such as were discussed in a previous section. The agreements in Tables I and II are quite satisfactory and show nothing which could be interpreted as real deviations between the experimental and the

[10] The values for P_{HBr}, P_{H_2}, P_{Br_2} are the partial pressures of the constituents at the end of a 10-hour period of irradiation as calculated from Lind and Livingston's Table III.

calculated values. However, in Table III, experiments 7, 11, 12, 15 and 16 are the least satisfactory. In 7, 11, 15 and 16 we are dealing with a large pressure of hydrogen and an appreciable amount of hydrogen bromide. In the synthesis experiment 11 we calculate too large a yield of hydrogen bromide and in the decomposition experiments we calculate too much decomposition of hydrogen bromide. The reaction which is most plausible to explain these discrepancies is:

$$H_2^+ + HBr \rightarrow H_2 + HBr^+ + 51 \text{ kcal.} \quad (8a)$$

Experiment 12 is particularly interesting because it is the only experiment in which P_{H_2} is very small and that of Br_2 and HBr are large. For this condition it will be seen that $(1-B)$ has the very small value 0.059. Therefore, the values of A and of b are not important. And since P_{H_2} is so small that it likewise cannot play an important role, we must, therefore, look for a reaction which decomposes HBr without the intermediate formation of H atoms. The possibility of Br_2^+ or Br^+ reacting with HBr would be inadequate to explain the observed yield unless they too decomposed HBr without the formation of atoms. The only reaction of this type is

$$HBr^+ + HBr \rightarrow H_2 + Br_2^+ - 7 \text{ kcal.} \quad (9)$$

and this seems to be ruled out of consideration from energy considerations if the ionization potentials of HBr and of Br_2 are respectively 13.2 ev and 12.8 ev. However, the fact that Br_2^+ does not increase the yield of HBr in a hydrogen bromide mixture indicates that the reverse reaction to (9) is prevented either by endothermicity or a high energy of activation.

The preceding theory could be experimentally tested if (*a*) a procedure could be devised of carrying the ions to metal electrodes where they would combine without reacting and then measuring the residual reaction due to excited molecules; (*b*) measuring the relative rates of reaction of electrons with Br_2 and HBr to make $Br + Br^-$ and $H + Br^-$ respectively.

The discrepancies in Table III between the calculated and measured M/N yields could probably be accounted for by a consideration of reactions of the type of (8a) and (9) but we have preferred to await further investigation making more certain the reality of these discrepancies before carrying our analysis further. While clustering no doubt occurs we have regarded it as playing a very minor role. Thus the activation energy of certain reactions may be increased or lessened by a sheath of molecules in much the same way as this is accomplished for ions in solution. However, the course of reaction of the ions is governed chiefly by the same type of specific considerations important in any gas phase reactions.

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The Vapor Pressure of Potassium Chloride and Caesium Iodide Crystals

V. Deitz,* *Department of Chemistry, University of Illinois*

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THE measurements of Rodebush, Murray and Bixler[1] of the electric moments of the alkali halide molecules attribute a value of roughly ten Debye units to these molecules. Since this high value for the dipole moment has been calculated on the assumption of simple diatomic moeculles, it is of importance to consider the possibility of association into at least double molecules, $(KCl)_2$. Such a molecule could conceivably have either a rhombic structure with a zero resultant moment or a linear structure with a corresponding large moment. If no association is present then the nearly 100 percent ionic nature of the alkali halide molecule is fairly well ascertained.

The vapor pressures were measured in a tem-

* National Research Fellow, 1935.

[1] Rodebush, Murray and Bixler, J. Chem. Phys. **4**, 372 (1936).

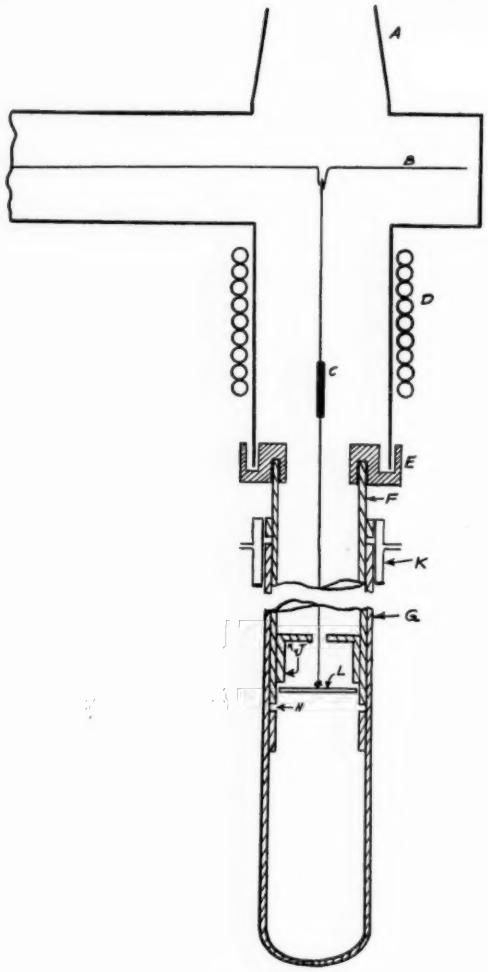

FIG. 1.

perature region comparable to that used in making the electric moment measurements cited above. The conditions in high temperatures (600–700°C) and low pressures (approximately 10^{-2} mm Hg) limit the number of methods available for making the measurements. The well-known molecular effusion method of Knudsen allows one to calculate the vapor pressure from the amount of vapor escaping through a hole in unit time, providing that the molecular weight is known. Since, in this investigation, the molecular weight is the unknown, it is necessary to measure the vapor pressure by an independent method.

The first attempt which was made to measure the absolute vapor pressure involved a molecular beam experiment. A molecular beam of the salt vapor was completely intercepted by a very thin aluminum vane which, in turn, was centered on a quartz fiber of about two μ diameter. The axis of rotation in the fiber was about one centimeter from the center of the beam. The torsional deflection of the quartz fiber was observed by means of a light beam reflected from a tiny mirror fastened at the center of the vane. Consistent data were obtained only after taking special precautions to avoid electrostatic charges. Unfortunately, these data must be considered untrustworthy in view of the following considerations. A salt molecule on collision with the cold aluminum vane sticks to it, thus transferring a momentum equal to mv. In addition some adsorbed air molecules are kicked off due to the heat of condensation, thus contributing an additional momentum to the vane. Since the vacuum was about 10^{-6} mm Hg, the aluminum was in all probability instantly covered with adsorbed air molecules. Hence, the pressures as measured must be considered as too high to an extent which is at present unknown.

The second attempt to measure the vapor pressure was by means of an adaptation of the absolute manometer of Rodebush and Coons.[2] This method was carried out to a successful conclusion and it is described below. Some words might be pertinent as to the accuracy of the data necessary to establish the presence of association. If the vapor were 100 percent associated, the pressure would only be decreased by the factor $\sqrt{2}$ over that of an unassociated vapor. Thus, if one wants to establish association to within ten percent, it is necessary that the vapor pressure data be accurate to wihin four percent. Hence, it seems advisable to take all data in the same apparatus in order to assure a dependable temperature scale in putting the data together.

A. The Vapor Pressure Measurements

The construction of the absolute manometer as used in this work is shown in Fig. 1.

Several attempts were made to make the apparatus of metal, but finally resort had made to an apparatus made of transparent vitreosil

[2] Rodebush and Coons, J. Am. Chem. Soc. **49**, 1953 (1927).

quartz. *L* is a disk of fused quartz about 2.5 cm in diameter, the upper surface of which is ground to seat on the ground end of the quartz tube *J*. *C* is a small needle of soft iron, enclosed in glass, and *B* is a cantilever arm made from a quartz fiber by which the system is suspended. *B* is about ten inches long from the point of suspension to the point of support, which is a quartz to Pyrex seal to the rest of the apparatus. The arm *B* extends outwards for about two inches past the suspension support and is pulled out to a fine point, the extreme tip being about a millimeter from a plane window. A microscope was then used to measure the position of the arm and hence give the vertical position of the quartz disk. *D* is a coil through which a current is passed to bring an electromagnetic traction on *C*, thus pulling the disk upward to seat on *J*.

The ground seat, *J*, is sealed within a transparent quartz tube *F*, 12 mm bore, the top of which is sealed to the remainder of the apparatus by a De Khotinsky joint at *E* in the manner shown. Surrounding the quartz tube *F* is another transparent quartz tube, *G*, 14 inches long, which is closed at the bottom. A short length of quartz tube of the same diameter as *F* is sealed within *G*. The seal is made at the bottom, the top end having been previously ground to make a seat with the bottom of the inner tube *F* at *H*. The salt crystals are placed at the bottom of the outside tube *G*. This is then slipped into place and sealed at *K* by means of a water-cooled picein joint. The long suspension is lowered into place through the opening of the ground joint at *A*. The female part of the joint carries a test tube sealed concentrically within it which serves as a liquid air cooled surface.

The bottom of the outer quartz tube *G*, loaded with the salt, is placed snugly into a block of nickel into the top and bottom of which were drilled two holes to receive thermocouples. The junctions of the thermocouples extend through and touch the quartz tube.

A superheating coil was placed directly on *G* in the region around the quartz disk. This coil serves to keep the temperature of the disk several degrees above that of the salt in order to prevent condensation of the vapor on the quartz disk and seat. Finally, a pot furnace is raised into position to surround the entire assembly.

Procedure

In operation no current is passed through the coil *D* and the system is evacuated to a pressure between 10^{-5} to 10^{-6} mm Hg. The salt is heated to within 50° of the point where the lowest pressure can be detected by the manometer. After 24 hours pumping the temperature is then raised and sufficient current is passed through the coil to seat the disk firmly on its seat. Time is allowed for pressure equilibrium to be established and then the current is decreased until the disk just drops from its seat on the end of the tube.

This "dropping current" is taken as the null-point and it was found to be reproducible. At the null-point the apparatus functions as an electromagnetic balance. The forces upwards consist of the tension in the quartz cantilever support, the magnetic pull of the solenoid, and the force due to the pressure of the vapor on the quartz lid, equal to the pressure times the area. The force downwards is the force of gravity. As the pressure increases, the pull necessary from the solenoid decreases. The data thus obtained for KCl and CsI at various temperatures are plotted in Figs. 2 and 3. At low temperatures one may observe

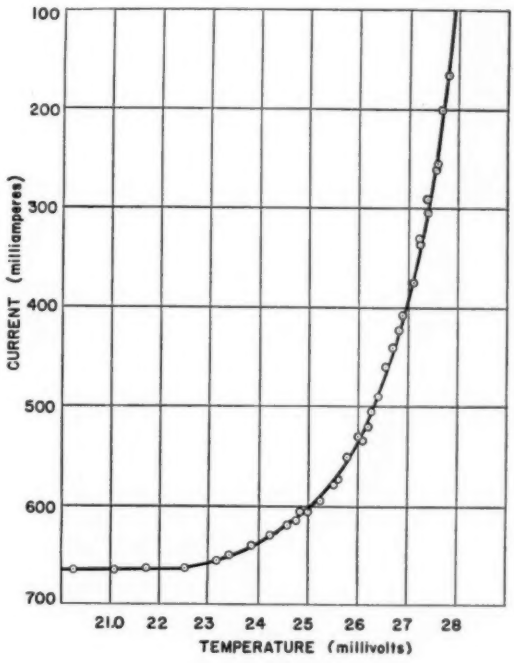

Fig. 2. KCl.

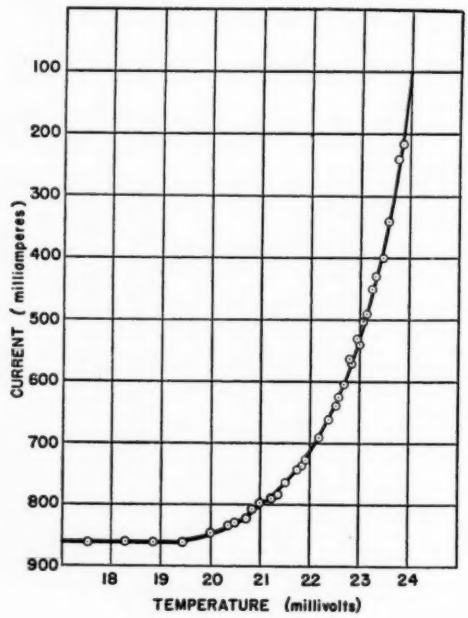

FIG. 3. CsI.

how the "dropping current" remains constant with temperature. Then as the temperature is raised, the curve pursues a typical vapor pressure plot. It was found that upon the first heating of the salts, the "dropping current" varied from ten to thirty percent higher than values obtained on subsequent heatings. This is attributed to adsorbed gases coming off of the salt crystals. The salt was fused preliminary to being placed in the apparatus and the fused mass broken up. It was then powdered in order to assure a sufficiently high rate of evaporation to maintain a saturated vapor. Because of this procedure the adsorbed gases mentioned above could not be avoided. All the remaining data are included in the graphs of Figs. 2 and 3; these show the consistency of the data during subsequent heatings and coolings of the salt.

The vapor pressures were calculated from the above data with the following calibration. The quartz disk was replaced by an aluminum pan and sufficient weights added to make the total weight equal the weight of the quartz disk. The necessary current was then passed through the solenoid to bring the pointed end of the cantilever arm B to the null-point position, previously observed with the quartz disk seated in place. By removing weights from the pan and observing the corresponding decrease in the solenoid current, a calibration was obtained. The calibration curve was found to be linear and of a slope corresponding to a sensitivity of 0.280 milligram per milliampere. The "null-point" of the apparatus was found to be independent of temperature in the region in which the measurements were made. This is attributed to the fact that both the suspension and the quartz tube carrying the ground seat were made out of the same material, namely transparent vitreosil, and hence had the same coefficient of linear expansion. An additional calibration was made against a McLeod gauge by using air in the apparatus with the same results. The thermocouples were calibrated against the freezing point of a sample of aluminum obtained from the Bureau of Standards.

RESULTS

The results are given in Table I and Table II. In addition, an empirical equation has been fitted to each set of data, the equation being linear in $\log_{10} P$ and $1/T$, cf., Figs. 4 and 5.

The heats of sublimation of KCl and CsI as

TABLE I. *Vapor pressure of KCl (crystal).*

Temp. °K	Pressure (dynes) Obs.	Calc.
847.2	1.35	1.33
855.6	1.89	1.80
879.4	3.95	4.08
892.1	6.22	6.08
903.8	8.86	9.07
910.0	11.10	11.04
918.0	13.8	14.1
929.1	20.3	19.9
936.2	24.9	24.6

$\Delta H_{\text{Sub}} = 51{,}800$ cal./mole,
$\log_{10} P_{\text{dynes}} = -11{,}300/T + 13.461$.

TABLE II. *Vapor pressure of CsI (crystal).*

Temp. °K	Pressure (dynes) Obs.	Calc.
767.2	2.03	1.95
785.8	4.00	4.05
801.8	7.45	7.44
807.9	9.60	9.30
816.3	12.5	12.6
823.0	16.3	16.0
830.3	20.5	20.6
840.5	29.3	29.3
846.8	36.4	36.2

$\Delta H_{\text{Sub}} = 47{,}500$ cal./mole,
$\log_{10} P_{\text{dynes}} = -10{,}360/T + 13.793$.

given by Mayer and Helmholz[3] compare very favorably with the above data, namely, 51,600 and 47,300 calories as compared with the experimental values of 51,800 and 47,500 calories, respectively. The correction to 0° is almost negligible.

When the vapor pressure data for liquid KCl [4] are extrapolated to the melting point, the plot is found to intersect the extrapolation of the above data for the solid at the temperature of 1095°K. This is less than five percent from the observed melting point of 1049°K, and is all that one can expect from an extrapolation over a temperature range of about 250°.

B. The Molecular Effusion Measurements

The Knudsen formula for molecular effusion may be written as follows

$$p=(w/t)(2RT/M)^{\frac{1}{2}}(1/A+3L/2\pi D^3),$$

where p is the pressure, w is the mass of vapor which passes in t seconds through an orifice of cross section A, of diameter D and of length L. M is the molecular weight and T the absolute temperature. By making a thin edged orifice in which L is between $D/5$ and $D/10$, one sees that the term $3L/2\pi D^3$ is only about five percent of $1/A$. The salts in these experiments were contained in small quartz capsules made in the following way.

A quartz tube with an inside diameter of two millimeters and a wall thickness of one millimeter was drawn down to a small constriction at one end. This constricted end was carefully heated; and just before the hole collapsed, a bubble of about six millimeters diameter was blown. With sufficient luck there was sometimes formed a small thin edged circular hole, situated at the top of the bubble. The diameter of this orifice was accurately measured with a microscope. By carefully grinding the edge of the circular hole the thickness was reduced to a value between one-fifth and one-tenth the diameter of the hole.

These quartz capsules were suspended in the vapor pressure apparatus described above, from which the quartz disk had been removed. While the temperature was attaining a constant value, the quartz capsule was lowered into a region 50° cooler than that to be used. At a stipulated time the capsules were lowered and rested on the bottom of tube G of Fig. 1. At the conclusion of the run the capsules were pulled up out of the heated part and the external furnace which surrounded the apparatus was immediately lowered. As the duration of the runs was from five to eight hours, the time is considered known to an accuracy better than one percent. The loss of weight of the quartz capsules was obtained by weighings on a Kuhlmann Micro Chemical Balance by Mr. K. W. Eder, microanalyst of the Chemistry Department.

The results are assembled in Table III. The area of the orifice was varied by a factor of ten as a test for saturation. Samples of powdered fused KCl and of KCl fused directly in the quartz tube gave the same results. Blank runs assured no appreciable evaporation losses of the quartz itself and served as controls in the micro balance weighings.

The purity of the salts used was tested. They were shown to be free from appreciable amounts of impurities.

[3] Mayer and Helmholz, Zeits. f. physik. Chemie **75**, 27 (1932).

[4] Rodebush and Fiock, J. Am. Chem. Soc. **48**, 2522 (1926).

Table III.

	T(°K)	t(sec.)	w(g)	$1/A+3L/2D^3$	P(single)	P(double)	P(obs.)
No. 1. KCl (fused)	932.0	14,540	0.010610	356.	21.0	14.9	21.5
No. 2. KCl (fused)	932.0	22,560	.016423	356.	20.9	14.8	21.5
			.010010	615.	22.0	15.5	
No. 3. KCl (powdered)	932.0	18,050	.006890	692.	21.2	15.0	21.5
No. 4. KCl (powdered)	913.1	21,600	.004465	692.	11.5	8.14	12.1
			.003557	952.	12.5	8.85	
No. 5. CsI	813.3	18,120	.005770	819.	10.6	7.50	11.0
			.006937	682.	10.7	7.35	
No. 6. CsI	789.3	21,600	.003097	819.	4.68	3.31	4.65
			.003683	682.	4.64	3.27	
No. 7. CsI	815.4	28,815	.004025	1970.	11.2	7.92	12.2
			.002500	3500.	12.3	8.70	

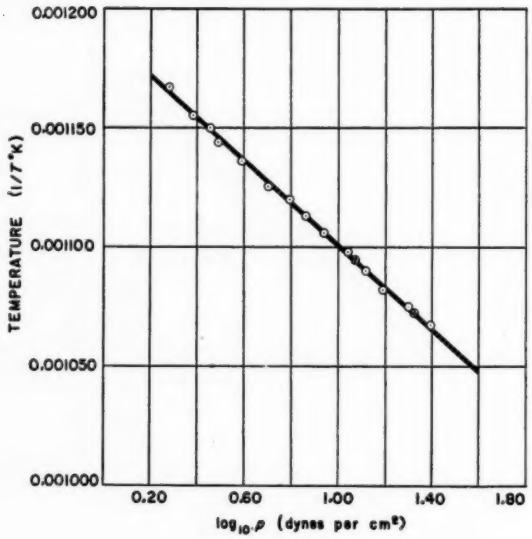

FIG. 4. KCl.

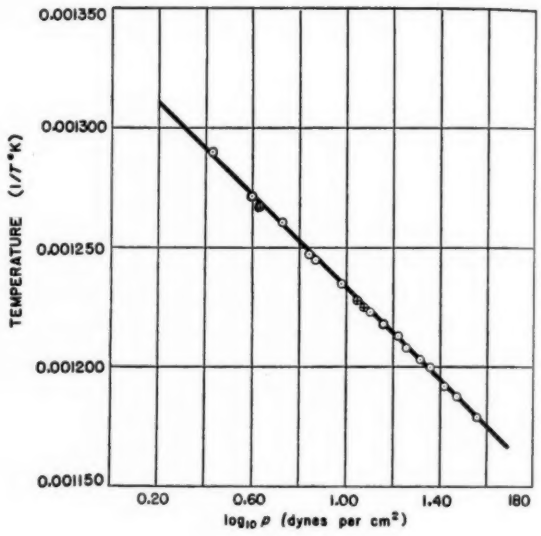

FIG. 5. CsI.

In columns 6 and 7 are the vapor pressures, calculated on the assumption of single and double molecules respectively. In column 8 are the corresponding pressures measured with the absolute manometer. Obviously single molecules are in the majority and one is able to say that to within an accuracy of ten percent the saturated vapor is not associated in the pressure region investigated. All the data are plotted in Figs. 4 and 5. The dots within circles are the absolute vapor pressure measurements and the crosses are the pressures calculated from the molecular effusion experiments.

DISCUSSION

The complete absence of association in the saturated vapor of molecules with such high dipole moments is somewhat surprising. If the heat of dissociation of the double molecule were small enough, the conditions of high temperature and low pressure would tend to prevent any association. Hence, one should further investigate the vapor for association at high pressures. But even at the higher saturated pressures it is doubtful whether the amount of association is ever very large. It can readily be shown that a large degree of association necessitates a large heat of dissociation of the double molecule into single molecules. A rough estimate is 75 kilocalories.

The heat of sublimation of KCl is in approximate figures 50 kilocalories. If this is really the heat of sublimation to $(KCl)_2$, then KCl gas would have 35 calories additional energy and would be 85 kilocalories above that of the crystal and, therefore, the heat of dissociation of KCl (g) into atoms must be only 65 instead of 101 kilocalories as calculated by Mayer and Helmholz[5] from Born cycle considerations.

Some preliminary theoretical calculations indicate that the heat of dissociation of the double molecules into single molecules might be as large as that estimated above. Using the newer values for the polarizability and the exponential repulsion potential of Born and Mayer[5] one obtains by use of the old method of Born and Heisenberg,[6] a value of 120 kilocalories for the heat of formation of KCl from ions. The calculated dipole moment is 8.23×10^{-18} e.s.u. This indicates that ionic forces predominate and by assuming Coulomb forces between two KCl molecules, a heat of dissociation of double molecules into single molecules of 75 kilocalories is obtained. The above calculation is being made the starting point of a perturbation calculation in anticipation of improving the agreement between theory and experiment.

The author wishes to express his appreciation to Professor W. H. Rodebush for his guidance in completing this research.

[5] Born and Mayer, Zeits. f. Physik **75**, 1 (1932).
[6] Born and Heisenberg, Zeits. f. Physik **23**, 404 (1924).

Relation of the States of the Carbon Atom to Its Valence in Methane

H. H. VOGE,* *Research Laboratory of Physics, Harvard University*

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An extended Heitler-London-Pauling-Slater calculation is given for methane. In addition to the usual quadrivalent configuration of the carbon atom, divalent and other configurations with which it may "resonate" are considered, in order to ascertain whether or not s^2p^2 carbon plays a more important part than usually is supposed. The mathematical formulation, an example of the use of the vector model, leads to a seventh degree secular equation, which is solved for empirical values of the integrals. The influence of resonance upon the energy is found to be small, but not negligible, and increases the stability of the molecule about 1.2 volts over the value for the usual Pauling-Slater configuration. The state of the carbon atom when it forms four electron-pair bonds is obtained explicitly in terms of the atomic states, and is found to comprise ^5S, ^3D and ^1D of sp^3, together with ^3P and ^1D of s^2p^2 and of p^4. This, the "valence state" of Van Vleck, is 7 volts above the ground state of the carbon atom; resonance lowers it about 2.5 volts. The resonance causes a greater modification in the wave function and in the valence state than it does in the energy. In the final section the relative energies of CH, CH_2, CH_3 and CH_4 are examined under the approximation of electron pairing, and are shown to have the regularly graded values of 4.0, 8.0, 12.1 and 17.0 volts when the experimental values for CH and CH_4 are used to determine the unknown integrals. There is no indication that CH_2 occupies a favored position, and the valence of four for carbon remains understandable in the light of the theory.

THE Heitler-London-Pauling-Slater theory of valence has been applied to a number of the problems arising for carbon compounds, and has proved fruitful in explaining observed properties. Van Vleck,[1] and Penney[2] have examined directional effects; Serber[3] has calculated the energies of hydrocarbons, and many other applications have been made,[4] with in general, good results. If these results are to retain validity, it must be shown that the methods of calculation are not subject to serious modifications. Now the usual theory assumes that for a valence of four the central carbon atom is in a configuration with four different orbits; that is to say, in an excited state. In no case has account been taken of the possible effect of other configurations, such as s^2p^2 for instance, which may "resonate" with the excited state and thereby enable the carbon atom to form more stable bonds. It is thus important to ascertain whether or not such low energy configurations alter appreciably the theoretical valence properties of carbon. A calculation designed to answer this question is given here. It should be noted that in any case the H-L-P-S method is far from perfect; but besides offering a simple picture of valence phenomena, it has qualitative significance and is important for the degree of valence.

Configurations considered

For convenience the calculation is based upon the four hybridized sp^3 tetrahedral wave functions: $t_i=\frac{1}{2}\psi(2s)+(3/4)^{\frac{1}{2}}\psi(2p\sigma_i)$, where $i=a$, b, c or d is one of the four tetrahedral directions, and $\psi(2p\sigma_i)$ means a $2p\sigma$ carbon wave function referred to the direction i. This involves no loss of generality, for four such orthogonal functions are just as good a system of reference as the usual s and p states. Three configuration types are considered: **A** that in which each of the four orbits is occupied by one electron, $t_at_bt_ct_d$; **B** those with one orbit occupied by two electrons, or filled, $t_a^2t_bt_c$, etc.; and **C** those with two filled orbits, $t_a^2t_b^2$, etc. **A** is the configuration usually used for quadrivalent carbon. As will be shown below, inclusion of **B** and **C** is equivalent to consideration of the carbon atom configurations s^2p^2, sp^3 and p^4.

The simplest quadrivalent carbon compound is methane, and it is the molecule treated. Hereafter **A**, **B** and **C** will signify the configuration of the complete molecule, including the four hydrogen orbits.

ENERGY MATRIX FOR METHANE

Number of symmetric states

The tetrahedral symmetry of CH_4 (point group T_d) causes considerable breaking-up of

* National Research Fellow in Chemistry.

[1] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933).

[2] W. G. Penney, Trans. Faraday Soc. **31**, 734 (1935).

[3] R. Serber, J. Chem. Phys. **3**, 81 (1935).

[4] See the monograph of J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935), for details and a review of the subject of quantum mechanical valence.

the energy matrix. Of chief interest is the segment of lowest energy, that involving the symmetric singlet states. The number of these states can be determined by general group theoretical methods.[5, 6, 7] For configuration **A**, with eight nonidentical orbits, the permutation degeneracy leads to 14 singlet states, as may readily be seen from the "branching diagram."[8] Eyring, Frost and Turkevich,[5] and Seitz and Sherman,[6] have solved the methane problem for this configuration, and have shown that only 3 of the 14 states transform according to the symmetric irreducible representation A_1 of T_d[9] and hence contribute to the lowest segment of the energy matrix. These authors have also given methods, based upon bond eigenfunctions, of finding the symmetric states. Perhaps the best way of determining the number of states of any symmetry is to use the permutation group characters, as formulated by Serber.[7] It leads to the results for CH_4 shown in Table I, from which it is seen that symmetry reduces a problem of the 86th degree to one of the 7th degree. To elucidate the table, it should be remarked that there are 12 configurations of the type **B**, and that each of these has 6 nonidentical orbits, and hence gives rise to 5 singlet states. From the total of 60 states only three independent symmetric states (representation A_1) can be formed, as is readily shown by group theoretical methods.[10] Similarly, the 6 configurations of the type **C**, with 4 nonidentical orbits, have 2 singlets apiece, and it can be shown that only one symmetric state derives from the 12 states which thus arise. The lowest segment of the energy matrix for the configurations **A**, **B** and **C** is therefore seen to involve seven states.

TABLE I. *Characters and irreducible representations of T_d for configurations of the methane molecule.*

Config.	E	$3C_2$	$6S_4$	$6\sigma_d$	$8C_3$	Irreducible representations
A	14	6	2	2	2	$3A_1+A_2+2E+T_1+T_2$
B	60	0	0	2	0	$3A_1+2A_2+5E+7T_1+8T_2$
C	12	4	0	0	0	$A_1+A_2+2E+T_1+T_2$

Construction of the symmetric states

A straightforward way to find the symmetric states is to employ the transformation matrices representing the permutations which correspond to operations of the point group in question. These matrices have been given for eight or fewer electrons by Serber.[7] However the symmetric states can also be found by other and more illuminating methods of the vector model without resorting to the matrices. Of course all variants of the vector model are very closely related; as methods of attack on the problem of permutation degeneracy they possess many advantages in elegance and simplicity. These advantages have been indicated by Van Vleck,[11] and by Serber.[7]

The various singlet states for an eight electron system are set up by taking all possible arrangements in the following scheme: The spins of the pairs of electrons 1 and 2, 3 and 4, 5 and 6, and 7 and 8 are coupled to 0 or 1. The resultants of the first and second pairs, and of the third and fourth, are then coupled to 2, 1 or 0; and finally the remaining two vectors are combined to give 0 resultant. The 14 states formed in such a fashion are the same as those used by Serber as a basis for the matrices representing the permutations, and are indicated schematically in Fig. 1. For configurations **B** and **C** the same states may be employed, but only those are allowed which have the spins of electrons in filled orbits coupled to zero. In all cases, the labels of the orbits and those of the electrons in them are taken to be the same.

With states constructed as outlined above, the simple rule[11] that states are antisymmetric for the

[5] H. Eyring, A. A. Frost and J. Turkevich, J. Chem. Phys. **1**, 777 (1933).
[6] F. Seitz and A. Sherman, J. Chem. Phys. **2**, 11 (1934).
[7] R. Serber, J. Chem. Phys. **2**, 697 (1934).
[8] See diagram on p. 192 of reference 4; also reference 11.
[9] The notation of R. S. Mulliken, Phys. Rev. **43**, 279 (1933), is used for group theoretical quantities. Note that the representation A_1 is not to be confused with the configuration **A**.
[10] The only class operations of T_d which do not transform all configurations of the type **B** into different configurations are E and $6\sigma_d$. They are thus the only classes which can have characters different from zero. E gives the character 5 for each configuration (cf. reference 8), and hence $12\times5=60$ for the sum. A typical element of the class $6\sigma_d$ leaves unchanged only 2 configurations out of the 12; the character for each is [2211] in the notation of reference 7. For $n=6$, $S=0$, [2211]=1, and thus the character for $6\sigma_d$ is 2. The characters for the reducible representation of the singlet states of configurations **B** are then 60, 0, 0, 2, 0, as given in Table I, and the number of times each irreducible representation occurs may be found by means of the usual formula.
[11] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

permutation of two orbits when the spins are coupled to 1, and symmetric when they are coupled to 0, together with judicious numbering of the electrons in the molecular array, suffices to determine all but one of the seven symmetric states for the three configuration types. By way of example, the construction of the three states for configuration **A** is sketched. Let the carbon orbits be denoted by 1, 3, 5, 7 and the hydrogen orbits bonded to them by 2, 4, 6, 8, respectively. Let the coupling scheme be as above, and consider the state where 1 and 2, and the three other pairs associated with the tetrahedral bonds, are coupled to zero. This is seen to be unchanged by any operation of T_d; it is a symmetric state, and in fact, that of electron pairing. By examination of Serber's matrices[7] it is found to be state number 14 in his notation and can be denoted by $\mathrm{I}=A\{14\}$. Next consider the six states wherein the spins of the pairs forming two of the bonds are coupled to 1, and those for the other two bonds are coupled to zero. These states are transformed into each other by the operations of T_d, and their sum forms the symmetric state II. In terms of Serber's states it is, when normalized, $\mathrm{II}=(1/\sqrt{6})(A\{6\}+A\{8\}+A\{9\}+A\{11\}+A\{12\}+A\{13\})$. The third state is built out of the three states which have all the bond pairs coupled to 1. Such a coupling leads to a four vector problem, and the transformations of the states cannot be obtained by simple rules. With the aid of the formulas for the coupling of four vectors, given by Johnson,[12] the transformations may be derived. However, the same information is contained in the matrices for the permutations. The generating elements of the group T_d, which are C_3 and a diagonal reflection, may be chosen as the permutations (135)(246) and (17)(28), with the orbits numbered as above. On multiplying the proper matrices to obtain the representations of these permutations, and noting that the states concerned are $\{1\}$, $\{2\}$ and $\{5\}$, it is found that $\mathrm{III}=(1/3)(2A\{1\}+\sqrt{5}A\{5\})$.

For configurations **B** and **C**, where carbon orbits are paired, a different labelling scheme is imperative if the same spin-coupling states are to be used. Such a scheme is: 1, 2, 5, 6 for the carbon orbits, and 3, 4, 7, 8 for the corresponding hydrogen orbits. This scheme is used exclusively hereafter. With it, and the simple rule cited above, the symmetric states of **B** and **C** are readily found; they are shown in (1). For actual calculation of the interconfigurational elements of the matrix, the states of **A** are referred to the basis for the new labelling scheme. This is readily done by noting that the necessary permutation of the orbits is (23)(67), and computing the transformation matrix. The old symmetric states in terms of the new basis are then found from the inverse transformation. The seven symmetric states of the three configuration types are

$$\begin{aligned}
\mathrm{I}&=(1/4)(3A\{5\}+\sqrt{3}A\{6\}\\
&\qquad+\sqrt{3}A\{13\}+A\{14\}),\\
\mathrm{II}&=(1/2\sqrt{6})(4A\{2\}-\sqrt{3}A\{5\}\\
&\qquad+A\{6\}+A\{13\}+\sqrt{3}A\{14\}),\\
\mathrm{III}&=(1/12)(8A\{1\}+\sqrt{5}A\{5\}-\sqrt{15}A\{6\}\\
&\qquad-\sqrt{15}A\{13\}+3\sqrt{5}A\{14\}),\\
\mathrm{IV}&=(1/\sqrt{12})\sum_{i=1}^{12}B_i\{14\},\qquad(1)\\
\mathrm{V}&=(1/\sqrt{12})(\sum_{i=1}^{6}B_i\{6\}+\sum_{i=7}^{12}B_i\{13\}),\\
\mathrm{VI}&=(1/\sqrt{12})(\sum_{i=1}^{6}B_i\{4\}+\sum_{i=7}^{12}B_i\{7\}),\\
\mathrm{VII}&=(1/\sqrt{6})\sum_{i=1}^{6}C_i\{14\}.
\end{aligned}$$

Here the orbital wave functions specifying the various configurations are, with the order of the electrons always 1 2 3 4 5 6 7 8,

$$\begin{aligned}
A&=t_at_bh_ah_bt_ct_dh_ch_d,\\
B_1&=t_at_ah_ah_bt_ct_dh_ch_d,\\
B_2&=t_at_ah_ah_ct_bt_dh_bh_d,\\
B_3&=t_at_ah_ah_dt_ct_bh_ch_b,\\
B_4&=t_bt_bh_bh_at_ct_dh_ch_d,\\
B_5&=t_bt_bh_bh_ct_at_dh_ah_d,\\
B_6&=t_bt_bh_bh_dt_ct_ah_ch_a,\\
B_7&=t_dt_bh_dh_bt_ct_ch_ch_a,\\
B_8&=t_at_dh_ah_dt_ct_ch_ch_b,\\
B_9&=t_at_bh_ah_bt_ct_ch_ch_d,\\
B_{10}&=t_ct_bh_ch_bt_dt_dh_dh_a,\\
B_{11}&=t_at_ch_ah_ct_dt_dh_dh_b,\\
B_{12}&=t_at_bh_ah_bt_dt_dh_dh_c,\\
C_1&=t_at_ah_ah_bt_bt_bh_ch_d,\\
C_2&=t_at_ah_ah_ct_ct_ch_bh_d,\\
C_3&=t_at_ah_ah_dt_dt_dh_ch_b,\\
C_4&=t_bt_bh_ch_bt_ct_ch_ah_d,\\
C_5&=t_bt_bh_dh_bt_dt_dh_ch_a,\\
C_6&=t_ct_ch_ah_bt_dt_dh_ch_d.
\end{aligned}\qquad(2)$$

The t_i are the tetrahedral carbon wave functions defined above; the h_i are the hydrogen orbits. t_a and h_a (and other orbits with identical sub-

[12] M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931).

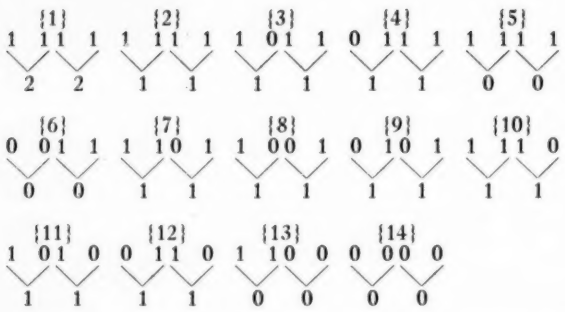

FIG. 1. The 14 spin coupling schemes for the singlets of eight electron systems. The four numbers forming the first rows are the resultants for the pairs 1 and 2, 3 and 4, 5 and 6, and 7 and 8 respectively, and are always kept in the same order in the figure. The final resultant (not shown) is of course 0.

scripts) always belong to the same tetrahedral direction a. Each of these configurations has singlet states, designated by $B_1\{14\}$, etc., according to the spin coupling scheme indicated in Fig. 1. Note that there are only two singlet states for the configurations **C**, but that they are numbered in accordance with the 14 states of **A**.

Calculation of matrix elements

The elegant matrix method of Dirac,[13] extended by Serber[14] to include several configurations, may be used to obtain the energy matrix. To secure the elements connecting the various states (1), formula (13) of reference 14 is used, together with the permutation matrices of reference 7. The fact that only symmetric states are involved facilitates determination of the elements. Thus for interactions between I and IV, only one configurational component of IV needs to be considered, since I is symmetric and would give the same result for any other component. If terms involving the squares of nonorthogonality integrals are neglected, only simple permutations need be included, except in those cases where identical orbits are interchanged. Under these conditions the energy matrix is found to be[15] as shown in Eq. (3).

Eq. (3). Energy matrix for methane. $H=$

	I	II	III	IV	V	VI	VII
I	$H_I^{AA}-3\gamma-3\beta+4\alpha-6\delta$	$(9/2)^{\frac{1}{2}}(\beta+\gamma-2\delta)$	0	$(3/2)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$(9/2)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$3(\theta-\kappa)$	$-(3/2)^{\frac{1}{2}}\mu$
II	$(9/2)^{\frac{1}{2}}(\beta+\gamma-2\delta)$	$H_I^{AA}-4\gamma-4\beta$	$(5/2)^{\frac{1}{2}}(\beta+\gamma-2\delta)$	$(3)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$H_I^{BA}-\theta-\eta-\kappa$	$(2)^{\frac{1}{2}}(\theta-4\eta+3\kappa)$	$-(3)^{\frac{1}{2}}\mu$
III	0	$(5/2)^{\frac{1}{2}}(\beta+\gamma-2\delta)$	$H_I^{AA}-\gamma-\beta-4\alpha-2\delta$	$(15/2)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$-(5/2)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$-(5)^{\frac{1}{2}}(\theta-\kappa)$	$-(15/2)^{\frac{1}{2}}\mu$
IV	$(3/2)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$(3)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$(15/2)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$H_I^{BB}+4\theta-2\mu-2\alpha-6\delta$	$-(3)^{\frac{1}{2}}(\delta-\alpha+2\eta-2\kappa)$	0	$-2(H_I^{BA}-\theta-\eta-\kappa)$
V	$(9/2)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$H_I^{BA}-\theta-\eta-\kappa$	$-(5/2)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$-(3)^{\frac{1}{2}}(\delta-\alpha+2\eta-2\kappa)$	$H_I^{BB}-2\gamma+8\theta-4\mu-2\beta-4\delta-4\eta$	$(8)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	0
VI	$3(\theta-\kappa)$	$(2)^{\frac{1}{2}}(\theta-4\eta+3\kappa)$	$-(5)^{\frac{1}{2}}(\theta-\kappa)$	0	$(8)^{\frac{1}{2}}(H_I^{BA}-\theta-\eta-\kappa)$	$H_I^{BB}-4\gamma+2\mu-2\beta-\alpha-3\delta-4\eta+4\kappa$	$2(6)^{\frac{1}{2}}(\eta-\kappa)$
VII	$-(3/2)^{\frac{1}{2}}\mu$	$-(3)^{\frac{1}{2}}\mu$	$-(15/2)^{\frac{1}{2}}\mu$	$-2(H_I^{BA}-\theta-\eta-\kappa)$	0	$2(6)^{\frac{1}{2}}(\eta-\kappa)$	$H_I^{CC}-4\gamma-2\alpha-6\delta$

[13] P. A. M. Dirac, *The Principles of Quantum Mechanics*, second edition, p. 222.

[14] R. Serber, Phys. Rev. **45**, 461 (1934).

[15] The actual calculation of the matrix elements is a little involved. The element I IV, for example, is not simply the interaction between states of two configurations **A** and **B**, but is the sum of the interactions of state I of **A** with certain states of the 12 configurations comprised in **B**. Furthermore, with the configurational wave functions as written in (2), higher permutations give rise to simple exchange integrals in some cases. To avoid the labor of computing the matrices for such higher permutations, the bases for the states of these configurations may be changed; that is to say, a new arrangement of the orbits may be taken. The old states in terms of those for the new arrangement are then found from the proper transformation matrix. Even after this is done, triple exchanges yield single exchange integrals for some interactions (B_1 with B_8 for instance). In such cases great care must be taken with the signs of the coefficients. (For sign conventions in linear transformations see E. Wigner, *Gruppentheorie*, p. 113 ff.) Finally it should be mentioned that in the matrix (3) certain dependent exchange integrals for the carbon orbits, which appeared originally, have been eliminated.

Here the integrals are

$$H_I^{AA}=(A|\boldsymbol{H}|A), \quad H_1^{CC}=(C_1|\boldsymbol{H}|C_i), \quad H_I^{BB}=(B_1|\boldsymbol{H}|B_1), \quad H_1^{BA}=(B_1|\boldsymbol{H}|A). \tag{4}$$

Also

$$\begin{aligned} \alpha&=(t_a h_a\,;\,h_a t_a), & \theta&=(t_a t_b\,;\,t_c t_a),\\ \beta&=(h_a h_b\,;\,h_b h_a) & \kappa&=(t_a h_c\,;\,h_c t_b),\\ \gamma&=(t_a t_b\,;\,t_b t_a), & \lambda&=(t_a t_b\,;\,t_a t_c),\\ \delta&=(t_a h_b\,;\,h_b t_a), & \mu&=(t_a t_b\,;\,t_c t_d),\\ \eta&=(t_a h_a\,;\,h_a t_b), \end{aligned} \tag{5}$$

where abbreviations of the type $(t_a h_a\,;\,h_a t_a)=(t_a(1)h_a(2)|\boldsymbol{H}|h_a(1)t_a(2))$ have been used.

The element $I\,I$ represents the approximation of electron pairing. The section involving the first three states (configuration **A**) yields the cubic secular equation given by Seitz and Sherman,[6] and, in a somewhat different form, by Eyring, Frost and Turkevich.[5] The numerical value of the complete matrix will be discussed in a later section.

Relation of Energy Matrix to the States of the Carbon Atom

Identification of the states contained

When the C−H and H−H integrals are set equal to zero, the matrix (3) depends only on the properties of the carbon atom, and yields seven atomic states. Symmetry considerations permit these states to be identified beforehand. It is only necessary to find what states of the C atom give rise to the symmetric representation A_1 of T_d when combined with four hydrogen orbits in a tetrahedral array.

The seven states for CH_4 were constructed so as to be symmetric (under the operations of T_d) in the orbital factor of the wave function. But they must also be symmetric in the spins, since the spin characters are the same as the orbit characters for even permutations,[16] and all the permutations of T_d for CH_4 are even (two electrons in each tetrahedral bond). By forming direct products of the representations of orbits for the carbon atom states and of those for four hydrogen orbits, and reducing the direct products, the possible representations of T_d for the orbital function of CH_4 are found. The same may be done with the spin functions. The carbon atom configurations which must be considered are those that can be used to construct sp^3 hybridized configurations; they are sp^3, and s^2p^2 and p^4 in equal amounts.

The orbital functions for the s^2p^2 and p^4 carbon states (which are *gerade*) of $L=0$ and 1 belong to the representations A_1 and T_1, respectively; and those for the sp^3 states (which are *ungerade*) of $L=0$, 1 and 2 to A_2, T_2 and $E+T_1$.[17] The representations for the transformations of the four hydrogen orbits are found by means of the characters for the symmetric permutation group,[18] and are A_2, T_1 and E when the spins are coupled to 2, 1 and 0, respectively. On reducing the direct products for combinations that can give rise to singlets for CH_4, it is found that the states ^3P and ^1D of s^2p^2 and p^4, and the states ^5S, ^3D and ^1D of sp^3 can each yield the representation A_1 once. With s^2p^2 and p^4 of equal rank, it is seen that there are just seven states in all. To clinch the identification, the spin functions must also be proven symmetric.

The representations of the spin functions for four electrons in a tetrahedral array are A_1, T_2 and E for $S=2$, 1 and 0, and are the same for both the carbon atom and the totality of the hydrogen orbits.[19] Reduction of the proper direct products (squares in this case) shows that any quintet, triplet or singlet state of the carbon atom can give rise to A_1 once and only once. Thus the seven states of the carbon atom which should be contained in the matrix (3) when interatomic terms are omitted are $s^2p^2\,{}^3P$, $s^2p^2\,{}^1D$, $sp^3\,{}^5S$, $sp^3\,{}^3D$, $sp^3\,{}^1D$, $p^4\,{}^3P$ and $p^4\,{}^1D$. The states which cannot participate in the carbon valences in CH_4 are $s^2p^2\,{}^1S$, $sp^3\,{}^3P$, $sp^3\,{}^3S$, $sp^3\,{}^1P$ and $p^4\,{}^1S$.

Transformation of matrix to form based on states of the carbon atom

By applying a canonical transformation to the energy matrix, it may be reduced to a form indexed by the seven carbon atom states listed above. The atomic states of interest are shown

[16] See for instance B. L. van der Waerden, *Die Gruppentheoretische Methode in der Quantenmechanik*, p. 135.

[17] R. S. Mulliken, Phys. Rev. **43**, 293 (1933), Table II.

[18] See R. Serber, reference 7. Also E. Wigner, *Gruppentheorie*, p. 149.

[19] The spin representations are readily found from those of the orbits by noting that the spin character is the same as that for the orbits for even permutations, and is of opposite sign for odd permutations, cf. reference 16.

in Table II in terms of the Slater parameters.[20, 21] The carbon integrals in terms of the same parameters are

$$\begin{aligned}
\gamma &= (1/16)[F_0(2s,2s)-2F_0(2s,2p)\\
&\quad +F_0(2p,2p)+4G_1+28F_2],\\
\theta &= (1/16)[F_0(2s,2s)-2F_0(2s,2p)\\
&\quad +F_0(2p,2p)-8F_2],\\
\lambda &= (1/16)[F_0(2s,2s)+2F_0(2s,2p)\\
&\quad -3F_0(2p,2p)-4G_1+12F_2],\\
\mu &= (1/16)[F_0(2s,2s)-2F_0(2s,2p)\\
&\quad +F_0(2p,2p)-4G_1+4F_2],\\
\chi &= (1/16)[F_0(2s,2s)+6F_0(2s,2p)\\
&\quad +9F_0(2p,2p)-4G_1-12F_2].
\end{aligned} \tag{6}$$

Further, the coulomb integrals for the carbon atom only are[22]

$$\begin{aligned}
H_I^{AA}(C) &= I(2s)+3I(2p)+6\chi,\\
H_I^{BB}(C) &= I(2s)+3I(2p)+6\chi+2\gamma-2\mu,\\
H_I^{CC}(C) &= I(2s)+3I(2p)+6\chi+4\gamma-4\mu,\\
H_I^{BA}(C) &= \tfrac{1}{4}I(2s)-\tfrac{1}{4}I(2p)+3\lambda+2\theta-2\mu.
\end{aligned} \tag{7}$$

When these quantities are substituted in (3), and interatomic terms are neglected, $\boldsymbol{H}(C)$, the matrix for the carbon atom, is obtained. A transformation R may then be found, such that $R^{-1}\boldsymbol{H}(C)R=\boldsymbol{H}'(C)$ has for diagonal terms the quantities listed in Table II, and only has non-diagonal elements (of magnitude G_1) connecting the interacting levels; i.e. connecting $s^2p^2\,{}^3P$ with $p^4\,{}^3P$, and $s^2p^2\,{}^1D$ with $p^4\,{}^1D$. In obtaining the transformation it is first convenient to note that $sp^3\,{}^5S$ is a root of the cubic equation for configuration A, as Van Vleck[23] has shown. After this term has been placed on the diagonal, the remaining sixth degree segment can be separated into parts corresponding to the triplets and singlets,[24] and these parts can be reduced individually. In this manner the complete transformation R is constructed.

With the aid of R the state of the carbon atom for electron pairing may be found in terms of the atomic states. Now the approximation of electron pairing is tantamount to the assumption that the element $I\,I$ of (3) is a factor of the entire matrix, and thus the state of the carbon atom in I is that for electron pairing. The inverse transformation R^{-1} gives the old states in terms of the new, and from it one finds that the state of the carbon atom when it forms four equivalent electron-pair bonds is

$$\begin{aligned}
I(C) &= \tfrac{1}{8}[-2\sqrt{5}(sp^3\,{}^5S)-3(p^4\,{}^3P)\\
&\quad -3\sqrt{2}(sp^3\,{}^3D)+3(s^2p^2\,{}^3P)+\sqrt{3}(p^4\,{}^1D)\\
&\quad +\sqrt{2}(sp^3\,{}^1D)-\sqrt{3}(s^2p^2\,{}^1D)].
\end{aligned} \tag{8}$$

This is the "valence state" of the carbon atom, defined by Van Vleck.[4, 23]

If the transformation R is applied to the complete matrix (3) a form is secured which displays the carbon atom energy levels. It is $\boldsymbol{H}'=R^{-1}\boldsymbol{H}R$, and is given in Eq. (9) (see next page).[24a] Here

$$\begin{aligned}
X &= H_I^{AA}+\tfrac{1}{8}[5F_0(2s,2s)+14F_0(2s,2p)\\
&\quad -19F_0(2p,2p)-4G_1-4F_2]+I(2s)-I(2p)
\end{aligned} \tag{10}$$

and

$$Z = M_{ss}-\tfrac{1}{3}M_{\sigma\sigma}-\tfrac{2}{3}M_{\pi\pi}. \tag{11}$$

The integrals M_{kk} are defined by

$$M_{kk}=\int\int\psi_k(1)h(2)\left[\frac{e^2}{r_{12}}-\frac{e^2}{r_{\mathrm{H1}}}\right]\psi_k(1)h(2)dv_1dv_2, \tag{12}$$

where $k=2s$, $2p\sigma$ or $2p\pi$ of C and the direction of reference for m_l is the C−H axis. $W(sp^3\,{}^5S)$ denotes the energy of the carbon level $sp^3\,{}^5S$ above the ground level $s^2p^2\,{}^3P$, etc. Hence $W(s^2p^2\,{}^3P)=0$.

Solution of the Secular Equation

Values of integrals

Instead of attempting to evaluate the integrals in (3) or (9), the procedure of assuming plausible values, and of treating certain integrals as adjustable parameters, is followed. This method probably exploits all the real information contained in a Heitler-London calculation; at any rate it is sufficient to give an unambiguous answer in the present case. The relative roots of

[20] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[21] To avoid fractional coefficients, the conventions of E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931), are used for the F's and G's.

[22] Here, and in Table II, $I(2s)$ and $I(2p)$ are not the I's defined by Slater (reference 20), but include the constant terms $W(C2s)$ and $W(C2p)$ respectively.

[23] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

[24] The multiplicities can be determined readily from the spin coupling scheme used in setting up the symmetric states.

[24a] The complete connections between (3) and (9) may be of value. Numerically $X=H_I^{AA}-9.75$ volts. H_I^{BB} and H_I^{CC} are the same as H_I^{AA} except for the carbon atom terms given in (7). $H_I^{BA}=H_I^{BA}(C)+Z$. H_I^{AA} is given explicitly in (18).

Eq. (9). $\mathbf{H}'=$

	I′	II′	III′	IV′	V′	VI′	VII′
I′	$X+W(sp^3\,{}^5S)$ $+\alpha+3\delta-6\beta$	$-(5/4)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	$-(5/2)^{\frac{1}{2}}(\delta-\alpha$ $+2\eta-2\kappa)$	$(5/4)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	0	0	0
II′	$-(5/4)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	$X+W(p^4\,{}^3P)$ $-4Z-4\delta+4\kappa$ -2β	$-(1/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	G_1	$(3)^{\frac{1}{2}}(\delta-\alpha$ $+2\eta-2\kappa)$	$(1/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	0
III′	$-(5/2)^{\frac{1}{2}}(\delta-\alpha$ $+2\eta-2\kappa)$	$-(1/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	$X+W(sp^3\,{}^3D)$ $-4\delta+4\kappa-2\beta$	$(1/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\delta+2\kappa)$	$(3/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	$\delta-\alpha$ $+2\eta-2\kappa$	$-(3/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$
IV′	$(5/4)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	G_1	$(1/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	$X+W(s^2p^2\,{}^3P)$ $+4Z-4\delta-8\eta$ $-4\kappa-2\beta$	0	$-(1/2)^{\frac{1}{2}}(\delta$ $-\alpha-2\eta$ $+2\kappa)$	$(3)^{\frac{1}{2}}(\delta-\alpha$ $+2\eta-2\kappa)$
V′	0	$(3)^{\frac{1}{2}}(\delta-\alpha$ $+2\eta-2\kappa)$	$(3/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	0	$X+W(p^4\,{}^1D)$ $-4Z-2\alpha-6\delta$ $+4\eta+4\kappa$	0	G_1
VI′	0	$(1/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	$\delta-\alpha+2\eta-2\kappa$	$-(1/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	0	X $+W(sp^3\,{}^1D)$ $-2\alpha-6\delta$	0
VII′	0	0	$-(3/2)^{\frac{1}{2}}(\delta-\alpha$ $-2\eta+2\kappa)$	$(3)^{\frac{1}{2}}(\delta-\alpha$ $+2\eta-2\kappa)$	G_1	0	$X+W(s^2p^2\,{}^1D)$ $+4Z-2\alpha-6\delta$ $-4\eta-4\kappa$

the secular equation depend only on the parameters describing the carbon atom, the quantity Z, β, and the C−H exchange integrals. The parameters for the carbon atom may be determined by empirical fitting of the energy levels, and from the theoretical calculations of Beardsley.[25] The values used are

$$F_0(2s,\,2s)=17.82 \text{ volts}, \quad F_0(2s,\,2p)=16.07, \quad F_0(2p,\,2p)=14.75 \tag{13}$$

from Beardsley's formulas, and

$$G_1=2.18 \text{ volts}, \quad F_2=0.188, \quad I(2p)-I(2s)=12.79 \tag{14}$$

from Van Vleck's[26] fitting of the sp^3 levels, together with the above values of the F_0's. Such values, when used in the formulas of Table II, reproduce the observed s^2p^2 and sp^3 levels quite well, as Van Vleck has shown; for the p^4 levels they give values about 1.4 volts above the energies computed by the Bacher-Goudsmit extrapolation method.[27]

TABLE II. *States of the carbon atom contained in the energy matrix for methane, in terms of the Slater parameters.*

State	Coefficient of:						
	$F_0(2s,\,2s)$	$F_0(2s,\,2p)$	$F_0(2p,\,2p)$	G_1	F_2	$I(2s)$	$I(2p)$
$p^4\,{}^1D$			6		−9		4
$p^4\,{}^3P$			6		−15		4
$sp^3\,{}^1D$		3	3		−6	1	3
$sp^3\,{}^3D$		3	3	−2	−6	1	3
$sp^3\,{}^5S$		3	3	−3	−15	1	3
$s^2p^2\,{}^1D$	1	4	1	−2	1	2	2
$s^2p^2\,{}^3P$	1	4	1	−2	−5	2	2

It is easy to show that Z vanishes identically if Slater's nodeless wave functions[28] are used, and if the same effective nuclear charges are used for the carbon $2s$ and $2p$ orbits. In any case Z should be small, and the value $Z=0$ may be assumed.

β is the same as the exchange integral for the hydrogen molecule, except for terms of the order of squares of nonorthogonality integrals, and is taken to be 0.9 of the Morse function for H_2. For CH_4, with C−H distance 1.09A, $\beta=-1.06$ volts.

The C−H integrals are related to the N_{kl} defined by Van Vleck[1, 23] as follows:

$$\begin{aligned}
\alpha&=-\tfrac{1}{4}[N_{ss}+3N_{s\sigma}+2\sqrt{3}N_{s\sigma}],\\
\delta&=-\tfrac{1}{4}[N_{ss}+\tfrac{1}{3}N_{s\sigma}-(4/3)^{\frac{1}{2}}N_{s\sigma}+(8/3)N_{\pi\pi}],\\
\eta&=-\tfrac{1}{4}[N_{ss}-N_{s\sigma}+(4/3)^{\frac{1}{2}}N_{s\sigma}],\\
\kappa&=-\tfrac{1}{4}[N_{ss}+\tfrac{1}{3}N_{s\sigma}-(4/3)^{\frac{1}{2}}N_{s\sigma}-(4/3)N_{\pi\pi}].
\end{aligned} \tag{15}$$

The N's have been discussed in some detail by Van Vleck, and by Penney.[29, 30] Two sets of

[25] N. F. Beardsley, Phys. Rev. **39**, 913 (1932).
[26] J. H. Van Vleck, J. Chem. Phys. **2**, 297 (1934); also reference 23.
[27] R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).
[28] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[29] W. G. Penney, Trans. Faraday Soc. **31**, 734 (1935).
[30] W. G. Penney, Proc. Roy. Soc. **A146**, 223 (1934).

values are considered in particular here:

$$N_{ss}=2,\ N_{s\sigma}=2.3,\ N_{s\sigma}=1.0,\ N_{\pi\pi}=-0.6, \quad (16)$$

from Van Vleck's illuminating treatment of CH_4;[23] and

$$N_{ss}=2.0,\ N_{s\sigma}=2.2,\ N_{s\sigma}=2.1,\ N_{\pi\pi}=-0.6, \quad (17)$$

taken from Penney,[29] who determined the most uncertain integral, $N_{s\sigma}$, by fitting the bending vibration frequency of methane.

Roots of the secular equation

With the values of the integrals defined above, the energy of the molecule for electron pairing (diagonal term $I\,I$ of (3)) is $X=2.12$ volts for choice (16), and $X-7.59$ for choice (17) of the N's. The lowest roots of the complete secular equation are[31] $X-3.50$ and $X-8.77$ volts for the two choices, and it is seen that the total energy of the molecule is lowered only 1.38 or 1.18 volts, respectively, by the influence of the other six states. The effect of states II and III in the cubic secular equation for configuration **A** was shown to be unimportant by Van Vleck.[23] Thus the small lowering of the energy is due principally to the configurations **B** and **C**, and there is a certain amount of resonance.

Other reasonable values of the N's lead to roots which are not much lower. Since electron pairing is a fairly good approximation, the secular equation in the form (3) may be solved by applying second order perturbation theory. This is readily done for a variety of cases. With the limits 1 volt and 2.5 volts for N_{ss} and $N_{s\sigma}$, and 1.5 and 2.5 for $N_{\sigma\sigma}$, no combination can be found which lowers the total energy more than two volts. The same approximation gives lowerings of 1.11 and 0.87 volts (instead of the accurate values 1.38 and 1.18) for the two particular cases (16) and (17). It therefore is apparent that the low energy configurations **B** and **C** of the central carbon atom are not very effective in increasing the binding energy in methane, and that the formula for electron pairing remains a moderately good approximation. However, although the energy is not greatly changed by the resonance, the wave functions and the promotional energy of the valence state are altered considerably.

Modification of the valence state by resonance

The wave functions for the lowest roots of the secular equation in the form (9) are shown for the choices (16) and (17) in Table III. The wave function for the state of electron pairing, (8), is also shown. The changes produced in the coefficients by the influence of the configurations B and C are quite appreciable and may be expected to modify the energy of the valence state. The energy of the carbon atom for electron pairing is known to be about 7 volts above $s^2p^2\ ^3P$ from Van Vleck's[23] analysis. It may of course also be found from (8) and the numerical values of the carbon atom energy levels (the interaction terms G_1 must be taken into account). The corresponding energies of the carbon atom in methane for choices (16) and (17) are found from the respective wave functions, and are 4.02 and 4.80 volts. The exact value for electron-pair bonds is 7.03 volts. Nevertheless, in spite of the 2.2 to 3 volts decrease in promotional energy, resonance increases the stability of the molecule by only 1.4 volts. Poorer bonding in the "divalent" configuration **B**, and in the "zerovalent" configuration **C** causes the compensation. However, the considerable change in the energy of the valence state indicates that too great a significance should not be attached to this quantity.

TABLE III. *Wave functions for the valence state of the carbon atom.*

State in (9)	Atomic state	Coefficients for:		
		Electron pairing	(16)	(17)
I′	$sp^3\ ^5S$	−0.559	−0.460	−0.445
II′	$p^4\ ^3P$	−.375	−.189	−.251
III′	$sp^3\ ^3D$	−.531	−.527	−.541
IV′	$s^2p^2\ ^3P$	.375	.539	.509
V′	$p^4\ ^1D$	.216	.132	.174
VI′	$sp^3\ ^1D$	.177	.145	.169
VII′	$s^2p^2\ ^1D$	−.216	−.382	−.358

RELATIVE ENERGIES OF CH_4, CH_3, CH_2 AND CH

The energy for CH_4 given by the single configuration which includes the state for four electron-pair bonds has proved to be roughly valid

[31] A convenient method of solving secular equations is that given by James and Coolidge, J. Chem. Phys. **1**, 834 (1933).

with respect to the possible interaction of other configurations. Corresponding approximations for single configurations may be used to determine the energies of CH_3, CH_2 and CH in terms of the same integrals defined for CH_4, and in this way relative energies for the four molecules may be secured. These quantities are of great importance in chemical kinetics, and are not known at all well experimentally, so that even rough estimates should be of value. Furthermore, such a comparison may be expected to shed light on the reasons for the quadrivalence of carbon.

In securing relative energies, the unknown integrals are treated as arbitrary parameters, and are used to fit the observed energies of CH_4 and CH. The integrals, and the C−H distances, are assumed to be the same for all four molecules.

CH_4

The electron pairing energy is, from (3),

$$W(CH_4)=H_I^{AA}-3\gamma-3\beta+4\alpha-6\delta$$
$$=I(2s)+3I(2p)+6\chi+4W(H)$$
$$+4K(CH_4)+6K(H_2)-3\gamma-3\beta+4\alpha-6\delta. \quad (18)$$

Here $K(CH_4)+(3/2)K(H_2)$ is one-fourth of the interactomic coulomb energy for CH_4, and

$$K(CH_4)=M_{ss}+M_{s\sigma}+2M_{\pi\pi}+V_{CH}$$
$$+\int h(1)\,V_C(1)h(1)dv_1, \quad (19)$$

where the M's are as in (12), V_{CH} is the potential energy between carbon and hydrogen centers, and V_C is the potential of the carbon center. $K(H_2)$ is the same as the coulomb energy for the hydrogen molecule, and is taken as 1/10 of the Morse function for H_2, $M(H_2)$. Thus $K(H_2)-(1/2)\beta=-0.35M(H_2)=0.41$ for CH_4.

On combining (6) and (15) with (18), it is found that the energy of formation of methane is[32]

$$W(CH_4)-W(C)-4W(H)=W_V(C)$$
$$+4K(CH_4)+6(0.41)+\tfrac{1}{2}N_{ss}$$
$$-(5/2)N_{s\sigma}-3\sqrt{3}N_{s\sigma}+4N_{\pi\pi}. \quad (20)$$

Here

$$W_V(C)=I(2p)-I(2s)+(1/16)[-13F_0(2s,2s)$$
$$-22F_0(2s,2p)+35F_0(2p,2p)-4G_1-76F_2]$$
$$=7.03 \text{ volts} \quad (21)$$

is the energy of the valence state of carbon, the value of which follows from (13) and (14); and $W(C)$ is $s^2p^2\,{}^3P$ as given in Table II, i.e., the energy of the normal carbon atom. $K(CH_4)$ may be estimated from Woods'[33] numerical calculation for CH_4. Subtraction of $(3/2)K(H_2)$ from his coulomb energy gives $K(CH_4)=-2.64$ volts. N_{ss}, $N_{s\sigma}$ and $N_{\pi\pi}$ are fairly well known, and are assumed to be 2.0, 2.3 and −0.6 volts, respectively. $N_{s\sigma}$ is then used to reproduce the observed energy of formation of methane. If the value $W(CH_4)-W(C)-4W(H)=-17.0$ volts[34] is adopted, then $N_{s\sigma}=1.69$, a figure which is between the value 1.0 determined by Van Vleck[23] on the assumption that the coulomb energy in CH_4 is four times that in CH, and the value 2.1 secured by Penney[29] from the vibration frequencies of CH_4. The new value of $N_{s\sigma}$, together with $K(CH_4)$, will be used to estimate the energies of formation of CH_3 and CH_2.

CH_3

This molecule is a seven electron problem, and ordinarily would involve 14 states for a Heitler-London treatment, but with the symmetry of the point group C_{3v}, the secular equation for the symmetric doublets is only of the fourth degree. The secular equation may be obtained for a carbon atom configuration with four different orbits, and conveniently be evaluated in two cases; (a) a right-angled model with the three hydrogens bound to three $p\sigma$ carbon orbits, and a free s orbit; and (*b*) a plane model, as formulated by Penney,[29] with three equivalent sp^2 hybridized wave functions at angles of 120° for the bonds, and a free p_π orbit. Electron pairing is found to be a good approximation in (b), but rather poor in (a). However the total binding is about 3 volts greater in (b) than in (a), so that Penney's conclusion that CH_3 is plane is substantiated, and the electron pairing formula may be employed. The energy of formation for plane CH_3 is

$$W(CH_3)-W(C)-3W(H)$$
$$=7.20+3K(CH_4)+3K(H_2)-(3/2)\beta$$
$$-(3/2)N_{s\sigma}-3\sqrt{2}N_{s\sigma}+3N_{\pi\pi}. \quad (22)$$

[32] Eq. (20) is the same as Van Vleck's (9) (cf. reference 23), except that W_{ion} has been omitted.

[33] H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932).

[34] This includes 1 volt of zero-point energy. It may be in error by as much as a volt because of the uncertainty of the heat of sublimation of carbon. See, V. Deitz, J. Chem. Phys. **3**, 58 (1935); R. Schmid, Zeits. f. Physik **99**, 274 (1936); G. Herzberg, Nature **137**, 620 (1936).

Here it is to be noted that the valence state, 7.20 volts above the ground state, is slightly different from that for CH_4. Using the values derived for CH_4, and noting that in this case $K(H_2)-(1/2)\beta = 0.34$, it is found that $W(CH_3)-W(C)-3W(H) = -12.12$ volts. This gives an energy of 4.88 volts for the reaction $CH_4 = CH_3 + H$, in agreement with the estimates of Mulliken[35] and Van Vleck.[23] The latter author has discussed the reasons for a difference of this order of magnitude, and little has been added here beyond an explicit formulation of the energy.

CH_2

For this molecule the carbon s^2p^2 configuration may be used. The resulting 4 electron problem gives rise to a quadratic equation; electron pairing is found to be a fair approximation to the accurate solution, the correction amounting to 0.4 volt. For right-angled CH_2 the energy formula is

$$W(CH_2)-W(C)-2W(H) = (3/2)F_2+2K(CH) + K(H_2)-(1/2)\beta+2N_{ss}-2N_{\sigma\sigma}+N_{\pi\pi}. \quad (23)$$

$$K(CH) = 2M_{ss}+M_{\sigma\sigma}+M_{\pi\pi}+V_{CH} + \int h(1)\,V_C(1)h(1)\,dv_1 \quad (24)$$

is the interatomic coulomb energy for CH. For the right-angled model assumed here, $K(H_2) - (1/2)\beta = +0.63$. Because M_{ss} is greater in absolute value (more negative) than $M_{\pi\pi}$, $K(CH)$ may be expected to be somewhat larger than $K(CH_4)$; the limiting value is obtained by setting $M_{\pi\pi}=0$, and is -4.0 if $K(CH_4) = -2.64$. $K(CH)$ is readily determined from the dissociation energy of CH. If the latter quantity is 3.7 volts,[36] $K(CH) = -3.38$; if it is 4.0 volts,[37] $K(CH) = -3.68$. The two cases give -7.45 and -8.05 volts for the energy of formation of CH_2 from the atoms, after the correction to the approximation of electron pairing has been applied.

CH

A quadratic equation gives the energy for CH; but electron pairing is found to be more than sufficiently accurate. The energy formula has been given by Van Vleck;[23] in the present notation it is

$$W(CH)-W(C)-W(H) = (3/2)F_2+K(CH) + N_{ss}-N_{\sigma\sigma}+\tfrac{1}{2}N_{\pi\pi}. \quad (25)$$

From this equation, and the dissociation energies, 3.7 or 4.0 volts, the values of $K(CH)$ used for CH_2 are obtained.

Discussion of relative energies

The estimated values 17.0, 12.1, 8.0 and 4.0 volts[38] for the energies of formation of CH_4, CH_3, CH_2 and CH form a well-graded series, and do not imply any special stability for the intermediate members. There is no indication that CH_2 occupies a favored position and that $W(CH_3)-W(CH_2)$ is only one or two volts, as has been supposed previously[39] from the fact that in CH_2 the carbon atom need not be promoted from the s^2p^2 state. The error in that supposition has been failure to recognize the fact that much stronger bonds can be formed once the central atom has been promoted, and that the promotion energy may well be offset by the greater bonding energy, as is seen to be the case for CH_3 and CH_4. Indeed, the bonding for hybridized orbits is so much more favorable than that for pure p orbits that CH_2 may perhaps be stabilized somewhat further by resonance involving excited configurations, an effect the very opposite of that invoked hitherto.

The relative energies are in accord with the experiments of Rice and co-workers[40] on the thermal decomposition of simple hydrocarbons. From a great wealth of experimental material, Rice concludes that the activation energies (which probably do not differ greatly from the dissociation energies) required to remove suc-

[35] R. S. Mulliken, J. Chem. Phys. **1**, 500 (1933).

[36] 3.5 volts given by H. Sponer (*Molekulspektren, I Tabellen* (1935)) plus ½ quantum of vibration.

[37] R. S. Mulliken, Rev. Mod. Phys. **4**, 80 (1932).

[38] In a paper which appeared after the work reported here had been completed, G. Nordheim-Pöschl (Ann. d. Physik **26**, 258, 281 (1936)) also gives estimates, likewise based on the Heitler-London theory, of the relative energies of CH_4, CH_3, CH_2 and CH. Her results are in good agreement with the above, although the method of approach is considerably different. Nordheim-Pöschl bases her calculations on the $s^2p^2\ ^3P$ and $sp^3\ ^5S$ states of the carbon atom, and does not take into account the other states that enter in (8) or Table III.

[39] R. Mecke, Zeits. f. Electrochemie **36**, 589 (1930); R. G. Norrish, Trans. Faraday Soc. **30**, 103 (1934).

[40] See F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (The Johns Hopkins Press, 1935).

cessive hydrogen atoms from methane are all 4 volts or more. This is in agreement with the energies given here; there are, however, conflicting bits of evidence[41] and the matter cannot be considered settled on the experimental side.

Errors involved

It may not be out of place to discuss briefly some of the possible errors and their implications. First of all, the N's have been assumed to be the same for all the molecules. Actually they are not, and the N's for molecules with many positive centers should be slightly greater than those for CH. This would increase the relative stability of CH_4 still further; however, the added terms are small, and probably do not play an important part. The assumption of constant C−H distances is borne out fairly well by the experimental data for CH_4 and CH.

The error involved in using the formula for electron pairing is known from the exact solutions of the secular equations. Only in the case of CH_2, where a correction has been applied, does the error exceed 0.1 volt.

Resonance, or the influence of other configurations, has been shown in the earlier sections to be of some importance in CH_4, where it contributes an additional 1.2 volts to the energy. It might be somewhat larger in CH_3, and strangely enough, perhaps still greater in CH_2. An electron pairing calculation for 120° CH_2 based on the same carbon configuration used for CH_3 yields an energy of 6.0 volts, which compares favorably with 7.4 or 8.0 volts for the molecule based on s^2p^2 carbon. A complication that would diminish the possible resonance arises from the fact that the most stable CH_2 based on an sp^3 configuration is linear (sp hybridized functions), whereas the most stable CH_2 based on s^2p^2 is right-angled (except for the small H−H repulsion). If resonance were taken into account, CH_2 would probably be found to have an angle intermediate between 90° and 180°, and a stability somewhat greater than that given above. Nevertheless, it is not likely that the relative energies would be modified to a very great extent by the inclusion of other configurations.

Finally, it must be admitted that the Heitler-London theory, when used for numerical calculations, has to a large extent the status of an empirical method. If nonorthogonality, higher exchanges and inner shells are included, the results obtained by direct evaluation of the integrals are worse than those yielded by the simple theory.[42] And furthermore, in that case so many integrals are introduced that they cannot effectively be treated as adjustable parameters. Use of the simple theory has led to a surprising number of valid results. As employed here it can at least be regarded as a powerful interpolation method.

In conclusion I should like to express my gratitude to Professor J. H. Van Vleck for suggesting this problem, and for many stimulating discussions.

[41] For instance, L. S. Kassel, J. Am. Chem. Soc. **57**, 833 (1935), and L. Belchetz, Trans. Faraday. Soc. **30**, 170 (1934), cite evidence supporting relatively greater stability for CH_2.

[42] Reference 4, pg. 192; A. S. Coolidge, Phys. Rev. **42**, 189 (1932); A. S. Coolidge and H. M. James, J. Chem. Phys. **2**, 811 (1934).

On the Theory of Dielectric Polarization

JOHN G. KIRKWOOD, *Department of Chemistry, Cornell University*

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The polarization of a nonpolar dielectric in a homogeneous field is investigated from a molecular point of view. A statistical calculation of the average local field in a molecule shows that fluctuations in the induced molecular moment give rise to a deviation from the Lorentz field. As a result, small but significant deviations from the Clausius-Mosotti formula are to be expected. A series expansion for $(\epsilon-1)v/3$ of the following form is obtained

$$(\epsilon-1)v/3=P_0[1+(1+\gamma+\sigma)P_0/v+\cdots],$$

where ϵ is the dielectric constant, v the molal volume and P_0 the molecular polarization. The coefficients in the corresponding expansion of the Clausius-Mosotti formula are all equal to unity. The correction γ, arising from translational fluctuations, is about 0.1 for most substances. The correction σ depends upon the optical anisotropy of the molecule and its shape.

INTRODUCTION

THE relation of the dielectric constant of a substance to the structural properties of its constituent molecules depends upon the average local field acting in the interior of a molecule. This average field is not in general equal to the field, **E**, entering into the macroscopic field equations, since **E** is obtained by averaging the local field in a different way, for example, over a physically small volume element, still large enough to contain many molecules. The classical method of Lorentz[1] provides an approximate estimate of the average local field in a molecule, which leads to the well-known Lorentz-Lorenz formula for the refractive index and to the Clausius-Mosotti formula for the dielectric constant. Lorentz actually calculated only the contribution to the internal field arising from external sources, and from the polarization of the molecules outside a spherical surface, of sufficient size to contain many molecules, and concentric with the molecule, in which the field is desired. Thus his result, $\mathbf{E}+4\pi\mathbf{P}/3$, is valid only if the contribution from the polarization of the other molecules in the spherical cavity vanishes. Lorentz did not attempt to give a general answer to this question. He demonstrated that the contribution from molecules inside the cavity vanishes in a cubic crystal, and remarked that it also vanishes in fluid for a random distribution of other molecules around the central one. These conclusions involve the implicit assumption that the electric moment of a molecule retains its average value through all phases of thermal motion. While this is doubtless an excellent approximation in crystals, it cannot be accepted without reservation for fluids. Keyes and Kirkwood[2] have pointed out that fluctuations in the induced moment of a molecule require a correction to the Lorentz field, $\mathbf{E}+4\pi\mathbf{P}/3$, and to the formulas based upon it. In the present article, we shall be concerned with an extended and more exact investigation of this question in nonpolar dielectrics. Since the approach is statistical and the dielectric is treated from the outset as a system of molecules, rather than a continuum, we do not need to employ the artifice of the Lorentz cavity at all.

We shall neglect the influence of molecular multipole moments of higher order than the dipole, as well as effects arising from inhomogeneity of the local field in the region occupied by a molecule. From the properties of spherical harmonics, it may be shown that these influences make no primary contribution to the average field, but at most can produce small corrections in the fluctuation terms to be calculated here. We also suppose the moment of a molecule to be equal to the product of its polarizability in vacuum and the average field acting in its interior. We thus assume no dependence of the molecular polarizability on the density of the dielectric. There is evidence from the Raman and absorption spectra of liquids, that this is not always a justifiable

[1] H. A. Lorentz, *Theory of Electrons*, p. 303.

[2] Keyes and Kirkwood, Phys. Rev. **37**, 202 (1931).

assumption, particularly for molecules having optically active infrared frequencies, which can make an appreciable contribution to the polarizability, for example carbon dioxide. Negative frequency shifts between gas and liquid in excess of the Lorentz-Lorenz shift[3] have been observed, which would tend to increase the contribution of infrared terms to the dispersion. A satisfactory treatment of this question demands a special investigation, which will be the subject of a later article.

Translational Fluctuations

In the present section, we shall confine our attention to a uniformly polarized dielectric, consisting of isotropic nonpolar molecules. We may suppose the dielectric to be bounded by two parallel planes, perpendicular to an applied homogeneous electrostatic field. These conditions are realized in the interior of an ordinary plane condenser.

The polarization, $\mathbf{P}$, is equal to average density of electric moment. If the dielectric consists of N molecules of a single species, occupying the volume v, we have

$$\mathbf{P}=N\bar{\mathbf{p}}/v, \tag{1}$$

where $\bar{\mathbf{p}}$ is the average electric moment of a molecule. Although all molecules have the same average moment, the electric moment $\mathbf{p}_i$ of any molecule i would be found to vary if followed through the phases of thermal motion of the system. With the neglect of electrical saturation effects and the influence of inhomogeneity in the local field, it is a sufficient approximation to write

$$\mathbf{p}_i=\alpha\mathbf{F}_i, \tag{2}$$

where α, the polarizability, is a molecular constant, and $\mathbf{F}_i$ is the field acting at the center of gravity of molecule i. The field $\mathbf{F}_i$ is produced in part by external charge distributions and in part by the electric moments of the remaining $N-1$ molecules. The contribution from external charge distributions, for example the surface charge on the plates of a plane condenser, is evidently equal to the dielectric displacement $\mathbf{D}$, defined* in the macroscopic theory as the field in an excised cavity of such a shape as to make the contribution from the polarization of the dielectric vanish. The dipole moment of each molecule k makes the following contribution to $\mathbf{F}_i$

$$\mathbf{p}_k\cdot\nabla_i\nabla_k(1/r_{ik}),$$

where r_{ik} is the distance between i and k, and ∇_i and $\nabla_k(=-\nabla_i)$ are the gradient operators associated with the coordinates of the centers of gravity of the respective molecules. The total field acting on i is therefore,

$$\mathbf{F}_i=\mathbf{D}-\sum_{\substack{k=1\\ \neq i}}^{N}\mathbf{T}_{ik}\cdot\mathbf{p}_k,$$
$$\mathbf{T}_{ik}=\nabla_i\nabla_k\left(\frac{1}{r_{ik}}\right)=\frac{1}{r_{ik}^3}\left[1-3\frac{\mathbf{r}_{ik}\mathbf{r}_{ik}}{r_{ik}^2}\right], \tag{3}$$

where $\mathbf{r}_{ik}$ is the vector distance between i and k and $\mathbf{T}_{ik}$ is a symmetric tensor operating on $\mathbf{p}_k$. It is convenient to express $\mathbf{T}_{ik}$ in dyadic form. Multiplication to the right or left with a vector signifies scalar multiplication with the right or left member of the vector pair in each term of the dyadic. The unit dyadic, $\mathbf{1}$, may be expressed as $\mathbf{s}_1\mathbf{s}_1+\mathbf{s}_2\mathbf{s}_2+\mathbf{s}_3\mathbf{s}_3$, where $\mathbf{s}_1$, $\mathbf{s}_2$, and $\mathbf{s}_3$ are any convenient set of mutually orthogonal unit vectors. In subsequent calculation, we shall find it convenient to choose $\mathbf{s}_1$, parallel to $\mathbf{D}$, and $\mathbf{s}_2$ and $\mathbf{s}_3$ in a plane parallel to the boundaries of the dielectric. From Eqs. (2) and (3) we obtain the following set of linear equations, which determine the electric moments $\mathbf{p}_1,\cdots\mathbf{p}_N$ as functions of the configuration of the centers of gravity of the N molecules

$$\mathbf{p}_i+\alpha\sum_{\substack{k=1\\ \neq i}}^{N}\mathbf{T}_{ik}\cdot\mathbf{p}_k=\alpha\mathbf{D}\quad i=1,\cdots N. \tag{4}$$

[3] Breit and Salant, Phys. Rev. **36**, 871 (1930); Salant and Sandow, Phys. Rev. **31**, 503 (1930); West and Arthur, J. Chem. Phys. **2**, 215 (1934).

* The statement that the contribution to the local field from the external charge distribution is equal to D is not always correct, but it is true in the interior of a homogeneous dielectric between charged plates, in which D is known to be equal to $4\pi\sigma$, where $\pm\sigma$ is the density of the surface charge on the plates. Moreover, there is no loss in generality in considering this case alone, for the relationship between the dielectric constant and molecular polarizability must be independent of the special type of field considered; so that it is sufficient to determine it for any particular field, to know it for all others. In electromagnetic theory, $\mathbf{D}$ is of course defined as $\mathbf{E}+4\pi\mathbf{P}$, or when $\mathbf{P}$ is linear in E and the dielectric is isotropic as $\epsilon\mathbf{E}$. If the dielectric is inhomogeneous, and if there are surfaces of discontinuity in its interior, D need not be simply the local field produced by the external distribution.

Solution of these equations together with a mean value operation would yield $\bar{\mathbf{p}}$, the mean moment of a molecule. We shall presently obtain a solution in powers of the polarizability α, the most convenient form for taking mean values. First, however, it is worth while to point out the relationship of the present method to the Lorentz theory.

We take mean values of both sides of Eqs. (4), remembering that $\alpha\mathbf{D}$ is a constant vector, with the result

$$\bar{\mathbf{p}}_i+\alpha\sum_{\substack{k=1\\ \neq i}}^{N}\overline{T_{ik}\cdot\mathbf{p}_k}=\alpha\mathbf{D}. \tag{5}$$

We now add and subtract a quantity $\alpha\mathbf{n}_i$ from the left side of Eq. (5), where $\mathbf{n}_i$ is a fluctuation, defined as follows.

$$\mathbf{n}_i=\sum_{\substack{k=1\\ \neq i}}^{N}[\overline{\mathbf{T}_{ik}\cdot\mathbf{p}_k}-\overline{\mathbf{T}_{ik}}\cdot\overline{\mathbf{p}_k}]. \tag{6}$$

Eq. (5) then becomes

$$\bar{\mathbf{p}}_i+\alpha\sum_{\substack{k=1\\ \neq i}}^{N}\bar{\mathbf{T}}_{ik}\cdot\bar{\mathbf{p}}_k+\alpha\mathbf{n}_i=\alpha\mathbf{D}. \tag{7}$$

Since the mean moments of all molecules of the homogeneous dielectric must have the same value $\bar{\mathbf{p}}$, we may write

$$\bar{\mathbf{p}}+\alpha\left(\sum_{\substack{k=1\\ \neq i}}^{N}\bar{\mathbf{T}}_{ik}\right)\cdot\bar{\mathbf{p}}+\alpha\mathbf{n}=\alpha\mathbf{D}. \tag{8}$$

The fluctuation $\mathbf{n}_i$ is of course the same for all molecules. It may be written in a slightly different form.

$$\mathbf{n}=\sum_{\substack{k=1\\ \neq i}}^{N}\overline{\mathbf{T}_{ik}\cdot(\mathbf{p}_k-\bar{\mathbf{p}})}. \tag{9}$$

It will vanish only if the moment $\mathbf{p}_k$ maintains its average value $\bar{\mathbf{p}}$ through all phases of thermal motion. This condition is not in general fulfilled in fluid dielectrics, although it probably is very nearly true in crystalline solids. We shall assume for the moment that the fluctuation $\mathbf{n}$ can be neglected. In this approximation, we have

$$\bar{\mathbf{p}}+\alpha\left(\sum_{\substack{k=1\\ \neq i}}^{N}\bar{\mathbf{T}}_{ik}\right)\cdot\bar{\mathbf{p}}=\alpha\mathbf{D}. \tag{10}$$

In fluid dielectrics, $\bar{\mathbf{T}}_{ik}$ has the same value for every molecular pair. A simple calculation yields (see appendix)

$$\bar{\mathbf{T}}_{ik}=\frac{4\pi}{v}\left(\mathbf{s}_1\mathbf{s}_1-\frac{1}{3}\right), \tag{11}$$

where $\mathbf{s}_1$ is a unit vector parallel to $\mathbf{D}$. From (10) and (11) we obtain

$$\left(1-\frac{4\pi N\alpha}{3v}\right)\bar{\mathbf{p}}+4\pi\frac{N\alpha}{v}(\bar{\mathbf{p}}\cdot\mathbf{s}_1)\mathbf{s}_1=\alpha D\mathbf{s}_1. \tag{12}$$

This vector equation yields the following scalar equations

$$\begin{gathered}(\bar{\mathbf{p}}\cdot\mathbf{s}_1)\left(1+\frac{8\pi N\alpha}{3v}\right)=\alpha D,\\ (\bar{\mathbf{p}}\cdot\mathbf{s}_2)=(\bar{\mathbf{p}}\cdot\mathbf{s}_3)=0,\end{gathered} \tag{13}$$

where $\bar{\mathbf{p}}\cdot\mathbf{s}_2$ and $\bar{\mathbf{p}}\cdot\mathbf{s}_3$ are the components of the average moment parallel to any pair of mutually orthogonal unit vectors in the plane perpendicular to $\mathbf{D}$. We then obtain the following expressions for $\bar{\mathbf{p}}$, the average molecular moment, and $\mathbf{P}$, the average polarization of the dielectric.

$$\begin{gathered}\bar{\mathbf{p}}=\frac{\alpha\mathbf{D}}{1+2P_0/v},\\ \mathbf{P}=N\bar{\mathbf{p}}/v=\frac{3}{4\pi}\frac{P_0/v}{1+2P_0/v}\mathbf{D}\\ P_0=4\pi N\alpha/3,\end{gathered} \tag{14}$$

where P_0 is the molecular polarization, N is Avogadro's number and v the molal volume. The macroscopic equations relating $\mathbf{P}$ and $\mathbf{D}$, and the dielectric constant ϵ are the following:

$$\mathbf{P}=((\epsilon-1)/4\pi)\mathbf{E},\quad \mathbf{D}=\epsilon\mathbf{E}. \tag{15}$$

Eqs. (14) and (15) lead to the expression

$$(\epsilon-1)/3=(P_0/v)/(1-P_0/v), \tag{16}$$

which is an alternative form of the Clausius-

Mosotti relation, usually written

$$[(\epsilon-1)/(\epsilon+2)]v=P_0. \tag{16a}$$

Thus when we ignore the fluctuation $\mathfrak{n}$ we are led to the result of the Lorentz theory, in which $\bar{\mathbf{F}}_i$ is calculated as the field at the center of an excised spherical cavity, the material in the cavity being assumed to contribute nothing.

The tensors $\mathbf{T}_{ik}$ may be regarded as the matrix elements of a linear transformation $\mathbf{T}$ in the $3N$ dimensional configuration space of the entire system, the electric moments $\mathbf{p}_i$ being the projections of a $3N$ dimensional vector on the subconfiguration space of molecule i. The solutions of Eq. (4) may then be written in the form

$$\mathbf{p}_i=(\mathbf{I}+\alpha\mathbf{T})^{-1}\alpha\mathbf{D}, \tag{17}$$

where $\mathbf{I}$ is the identity transformation. There are a number of ways of calculating $(\mathbf{I}+\alpha\mathbf{T})^{-1}$, the most common method leading to usual determinantal solution of a set of inhomogeneous linear equations. In order to facilitate the subsequent calculation of mean values, we shall find it convenient to expand $(\mathbf{I}+\alpha\mathbf{T})^{-1}$ in powers of α

$$(\mathbf{I}+\alpha\mathbf{T})^{-1}=\sum_{n=0}^{\infty}(-\alpha)^n\mathbf{T}^n. \tag{18}$$

With this expansion, the solutions of Eq. (4) take the following form

$$\mathbf{p}_i=\alpha\{\mathbf{1}-\alpha\sum_{\substack{k=1\\ \neq i}}^{N}\mathbf{T}_{ik}+\alpha^2\sum_{\substack{k,\ l=1\\ k\neq i,\ l\neq k}}^{N}\mathbf{T}_{ik}\cdot\mathbf{T}_{kl}+\cdots\}\cdot\mathbf{D}. \tag{19}$$

These solutions may be easily verified by applying the method of successive substitutions to Eqs. (4).[4] The mean value of $\mathbf{p}_i$ may then be written

$$\bar{\mathbf{p}}_i=\alpha\{\mathbf{1}-\alpha\sum_{\substack{k=1\\ \neq i}}^{N}\bar{\mathbf{T}}_{ik}+\alpha^2\sum_{\substack{k,\ l=1\\ k\neq i,\ l\neq k}}^{N}\overline{T_{ik}\cdot T_{kl}}+\cdots\}\cdot\mathbf{D}. \tag{20}$$

[4] See Courant and Hilbert, *Methoden der Mathematischen Physik* I, Kap. I, §2. The sufficient condition for convergence given there is not a necessary one. We shall assume convergence of (17) except for rare configurations, which make no finite contribution to mean values. The series will of course diverge on the null set of configurations, which make the determinant of $\mathbf{T}$ vanish. Other configurations for which it diverges will generally have zero probability because of molecular repulsive forces.

The fluctuation $\mathfrak{n}$ may be similarly expanded in powers of α, with the use of (19).

$$\mathfrak{n}=-\alpha^2\sum_{\substack{k,\ l=1\\ k\neq i;\ l=k}}^{N}[\overline{\mathbf{T}_{ik}\cdot\mathbf{T}_{kl}}-\bar{\mathbf{T}}_{ik}\cdot\bar{\mathbf{T}}_{kl}]\cdot\mathbf{D} \tag{21}$$

$$+\alpha^3\sum_{\substack{k,\ l,\ s=1\\ \neq i\ \neq k\ \neq l}}^{N}[\overline{\mathbf{T}_{ik}\cdot\mathbf{T}_{kl}\cdot\mathbf{T}_{ls}}-\bar{\mathbf{T}}_{ik}\cdot\overline{\mathbf{T}_{kl}\cdot\mathbf{T}_{ls}}]\cdot\mathbf{D}+\cdots.$$

We shall undertake the calculation of mean values for a fluid represented by a classical canonical ensemble. The mean value of any function $G_{ik\cdots l}$ of the relative coordinates of a group of $n+1$ molecules may be calculated from the formula

$$\bar{G}_{ik\cdots l}=\frac{1}{v^n}\int\cdots\int G_{ik\cdots l}e^{-\beta W_{ik\cdots l}}dv_k\cdots dv_l. \tag{22}$$

The potential of the average force, $W_{ik\cdots l}$, acting on the molecules of the group is given by

$$e^{-\beta W_{ik\cdots l}}=\frac{v^n\int\cdots\int e^{-\beta V_N}dv_1\cdots dv_{N-n-1}}{\int\cdots\int e^{-\beta V_N}dv_1\cdots dv_{N-1}}, \tag{23}$$

where V_N is the potential of the intermolecular forces in the entire system and β is equal to $1/kT$. The integration in the numerator extends over the configuration space of all molecules except those of the group, while in the denominator it extends over the configuration space of all molecules except any single molecule i of the group.[5] It is apparent that we may calculate mean values with the distribution functions valid in the absence of the external field D, since they are to be multiplied by D in the expressions for $\bar{\mathfrak{p}}$ and $\mathfrak{n}$, and we are neglecting powers of D higher than the first. The mean value, $\bar{\mathbf{T}}_{ik}$, given in Eq. (9) is independent of the magnitude and form of the average force potential W_{ik}. This is not true of the mean values of products, $\overline{\mathbf{T}_{ik}\cdots\mathbf{T}_{ls}}$. We have undertaken the calculation of the first term in the expansion of $\mathfrak{n}$, Eq. (21) for a fluid consisting of spherical molecules, exerting no attractive forces upon one another. For such a system, a rather tedious calculation yields (see appendix)

[5] See R. H. Fowler, *Statistical Mechanics* (Cambridge Univ. Press), p. 181. J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).

$$\overline{\mathbf{T}_{ik}\cdot\mathbf{T}_{kl}}-\bar{\mathbf{T}}_{ik}\cdot\bar{\mathbf{T}}_{kl}=-\frac{5\pi^2}{3v^2}\mathbf{1};\quad l\neq i;$$
$$\overline{\mathbf{T}_{ik}\mathbf{T}_{ki}}=\overline{\mathbf{T}_{ik}{}^2}=\frac{16\pi^2N}{9bv}\mathbf{1};\quad b=2\pi Na^3/3, \tag{24}$$

where a is the diameter of a molecule. In the double sum of the first term of Eq. (21), there are $(N-1)(N-2)$ terms in which l is different from i and $N-1$ terms in which l is identical with i. Approximating these numbers by N^2 and N,

$$\mathbf{n}=-(16\pi^2/9b-5\pi^2/3v)N^2\alpha^2\mathbf{D}/v. \tag{25}$$

The calculation of the higher order fluctuations becomes very complicated and has not been undertaken here. We may calculate $\bar{\mathbf{p}}$ either from Eqs. (8), (11) and (25) or directly from Eqs. (11), (20) and (24). If the former equations are used, the result must be expanded in powers of α, since we are not justified in retaining powers of α higher than the third in the expression for $\bar{\mathbf{p}}$, if powers of α higher than the second are discarded in $\mathbf{n}$. The result of either calculation is (see appendix)

$$\bar{\mathbf{p}}=\alpha\left[1-\frac{8\pi N\alpha}{3v}+\left(\frac{16\pi^2}{9b}-\frac{49\pi^2}{9v}\right)\frac{N^2\alpha^2}{v}+\cdots\right]\mathbf{D}. \tag{26}$$

Eqs. (1) and (26) together with the macroscopic Eqs. (13) allow one to express the dielectric constant as a function of α. Expansion of the result in powers of α yields

$$\frac{\epsilon-1}{3}v=P_0\left\{1+(1+\gamma)\frac{P_0}{v}+\frac{1}{16}\frac{P_0^2}{v^2}+\cdots\right\}, \tag{27}$$
$$\gamma=P_0/b.$$

Although this is actually a power series in P_0 or α, it is convenient to arrange it in powers of $1/v$. The coefficients of $1/v$ and $1/v^2$ are therefore not complete but from dimensional considerations, it is easily seen that the neglected terms must be of the types $P_0{}^n/vb^{n-1}$ and $P_0{}^n/v^2b^{n-2}$, respectively, where n is greater than two. When van der Waals forces of the attractive type, varying as the inverse sixth power of the intermolecular distance are introduced, the term γ is modified[6] as follows (see appendix)

$$\gamma=P_0/b(1+(A/3bRT)), \tag{28}$$

where A is the cohesive pressure constant in the van der Waals equation of state,

$$p=RT/(v-b)-A/v^2.$$

In order to compare Eq. (27) with the Mosotti formula, we expand the latter, Eq. (16), in a power series in P_0.

$$\epsilon-1v/3=P_0[1+P_0/v+P_0{}^2/v^2+\cdots]. \tag{29}$$

It is seen that the two series (27) and (29) agree only in their first terms. The coefficient of $1/v$ in Eq. (27) differs from that of Eq. (29) by a factor $(1+\gamma)$, and the coefficients of $1/v^2$ differ widely. Actually, for most nonpolar substances, P_0/v is so small even at liquid densities, that the term in $(P_0/v)^2$ is practically negligible in either Eq. (27) or Eq. (29). This is true in all of the experimental tests of the Clausius-Mosotti relation on compressed gases, so that in reality only the first two terms of Eq. (29) have been tested. Moreover where the relation has been confirmed, as for the fixed gases N_2, O_2, H_2, calculation shows the fluctuation correction to be within experimental error.[7] In general the fluctuation term γ causes a positive deviation from the Mosotti formula. Such a deviation has been observed by Uhlig, Kirkwood and Keyes, and has been confirmed by measurements of Oncley on carbon dioxide and propane.[8] The latter results will be discussed in detail in a forthcoming article by Oncley. His measurements lead to values of γ, agreeing tolerably well with those calculated from Eq. (28) with known equation of state constants. In general the experimentally determined values of γ are somewhat larger than the calculated ones. This suggests the presence of another effect, namely a variation of the polarizability with density. (See Table I.)

[6] The quantity γ corresponds to λ_0/P_0, where λ_0 is the fluctuation constant in Keyes-Kirkwood equation, as may be verified by calculating the expansion of $(\epsilon-1)v/3$ from this equation. γ differs from λ_0/P_0 by a factor 5/2, a discrepancy arising from a faulty calculation of $\mathbf{T}_{ik}{}^2$ in the earlier paper. There the influence of component of the electric moment in the plane perpendicular to D on the fluctuation was neglected. Although this component vanishes in the mean, its contribution to the mean square of the field does not.

[7] Tangl, Ann. d. Physik **10**, 748 (1903); **23**, 559 (1907); **26**, 59 (1908); Occhialini, Physik. Zeits. **6**, 669 (1905); Uhlig, Kirkwood and Keyes, J. Chem. Phys. **1**, 155 (1933).

[8] Uhlig, Kirkwood and Keyes, J. Chem. Phys. **1**, 155 (1933). Oncley, unpublished work.

TABLE I*

	P_0(cc)	b(cc)	A(cc² atmos.)·10^{-6}	γ(0°C)
N_2	4.38	50.5	1.34	0.121
O_2	3.95	46.2	1.49	.127
H_2	2.10	21.0	0.20	.114

* The equation of state constants were taken from Beattie and Bridgeman, Proc. Am. Acad. **63**, 229 (1928).

ANISTROPY AND ROTATIONAL FLUCTUATIONS

Raman and Krishnan[9] have discussed in a general manner the influence of molecular anisotropy on the polarization of a dielectric. They regard the molecule as constituting a cavity of arbitrary shape in a statistical continuum. Even though the polarization field in such a cavity were identical with the Lorentz field, when averaged over all molecular orientations, the average molecular moment induced by the polarization field need not be $(\mathbf{E}+4\pi\mathbf{P}/3)\bar{\alpha}$ where $\bar{\alpha}$ is the mean polarizability. This arises from the fact that the average moment is the mean value of the product of the polarizability tensor and the polarization field. Unless the molecule is optically isotropic or spherical in shape, both of these quantities depend upon molecular orientation, so that the mean value of their product over all orientations is not in general equal to the product of their mean values. This is a type of fluctuation different from the one considered in the previous section. Without detailed calculation, Raman and Krishnan observe that if the shape of the molecule corresponds qualitatively to its polarization ellipsoid, a negative deviation from the Mosotti formula will result.

We shall develop this idea in somewhat more detail on the basis of the method used in the previous section. For optically anisotropic molecules, Eqs. (4) become

$$\mathbf{p}_i+\sum_{\substack{k=1\\ \neq i}}^{N}\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}\cdot\mathbf{p}_k=\boldsymbol{\alpha}^{(i)}\cdot\mathbf{D}, \tag{30}$$

where $\boldsymbol{\alpha}^{(i)}$ is the polarizability tensor, and depends upon the orientation of i. If $\mathbf{n}_1^{(i)}$, $\mathbf{n}_2^{(i)}$, and $\mathbf{n}_3^{(i)}$ are unit vectors defining the principal optical axes of molecule i, $\boldsymbol{\alpha}^{(i)}$ may be written in dyadic form as follows

$$\boldsymbol{\alpha}^{(i)}=\sum_{s=1}^{3}\alpha_s\mathbf{n}_s^{(i)}\mathbf{n}_s^{(i)}, \tag{31}$$

where α_1, α_2, and α_3 are the principal polarizabllities of a molecule. Solution of these equations and averaging over all molecular orientations as well as over all configurations of the molecular centers of gravity leads to equations similar to Eq. (20).

$$\begin{aligned}\bar{\mathbf{p}}_i&=\bar{\alpha}\mathbf{D}-\sum_{\substack{k=1\\ \neq i}}^{N}\overline{\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}}\cdot\mathbf{D}\\ &\quad+\sum_{\substack{k,\,l=1\\ i\neq k}}^{N}\overline{\boldsymbol{\alpha}^{(i)}\cdot T_{ik}\cdot\boldsymbol{\alpha}^{(k)}\cdot T_{kl}}\cdot\mathbf{D}+\cdots,\\ \bar{\alpha}&=(\alpha_1+\alpha_2+\alpha_3)/3.\end{aligned} \tag{32}$$

The mean value $\boldsymbol{\alpha}^{(i)}\mathbf{T}_{ik}$ for a molecule of arbitrary shape may be calculated. (see appendix)

$$\overline{\alpha^{(i)}\cdot T_{ik}}=4\pi\bar{\alpha}\mathbf{s}_1\mathbf{s}_1-\frac{4\pi}{3}\sum_{l=1}^{3}\alpha_l J_l\mathbf{1}, \tag{33}$$

$$J_l=-\frac{1}{4\pi}\int\nabla\left(\frac{1}{r}\right)\cdot\mathbf{n}_l\mathbf{n}_l\cdot d\mathbf{A},$$

where the integrals are to be extended over the surface of a molecule with outwardly directed normal. This expression becomes identical with Eq. (11) if the molecule is optically isotropic $(\alpha_1=\alpha_2=\alpha_3=\bar{\alpha})$ or if it is spherical in shape. With some algebraic transformations similar to those used in the foregoing section, we obtain the following expansion for $(\epsilon-1)v/3$.

$$\begin{aligned}((\epsilon-1)/3)v&=P_0[1+(1+\gamma+\sigma)(P_0/v)+\cdots],\\ \sigma&=(1/3\bar{\alpha})[(\alpha_1-\alpha_2)(J_1-J_2)\\ &\quad+(\alpha_1-\alpha_3)(J_1-J_3)+(\alpha_2-\alpha_3)(J_2-J_3)],\\ \gamma&=(3v/4\pi\bar{\alpha})\overline{\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}\cdot\boldsymbol{\alpha}^{(k)}\cdot\mathbf{T}_{ki}},\end{aligned} \tag{34}$$

where γ is the part of the fluctuation arising from the diagonal terms of the double sum in Eq. (32). We do not attempt to carry the expansion to terms in $1/v^2$ as in the case of isotropic spherical molecules, but we may assume that this term will not differ in magnitude from $1/16(P_0/v)^2$.

[9] Raman and Krishnan, Proc. Roy. Soc. **A117**, 589 (1927).

Since γ itself is of the nature of a small correction, we are justified in neglecting optical anisotropy in calculating it. With this approximation, we may write

$$\gamma=\frac{3\bar{\alpha}}{2\pi}\int_0^\infty \frac{1}{r^6}e^{-\beta\overline{W}}dv, \tag{35}$$

where $\overline{W}$ is the potential of the force acting between a pair of molecules, averaged over all configurations of the other molecules, and over the orientation of one member of the molecular pair. The shape of the molecule is of course reflected in the potential $\overline{W}$, $e^{-\beta\overline{W}}$ vanishing within a cavity of dimensions determined by molecular repulsion. The integral in Eq. (35) is not extremely sensitive to the form of the cavity of exclusion, so that the fluctuation γ will be approximately given by Eq. (28) even for nonspherical molecules. The term σ has been calculated for a molecule having the shape of an ellipsoid of rotation, its axes being assumed to coincide with the principal optical axes of the molecule. If α_1 is the polarizability along the major axis and α_2 the value of the other two principal polarizabilities, we have

$$\sigma=\frac{2}{3}\frac{\alpha_1-\alpha_2}{\alpha}\left[\frac{1-e^2}{e^3}\sinh^{-1}\frac{e}{(1-e^2)^{\frac{1}{2}}}-\frac{1-e^2}{e^2}-\frac{1}{3}\right], \tag{36}$$

where e is the eccentricity of the ellipse. For extremely elongated molecules, σ approaches the value

$$\sigma_0=-2(\alpha_1-\alpha_2)/9\bar{\alpha}, \tag{37}$$

corresponding to unit eccentricity. For a ratio of minor to major axis of 1/3, the numerical factor of $(\alpha_1-\alpha_2)/\bar{\alpha}$ is about 2/3 of the σ_0 value. If the polarizabilities of the molecule correspond in magnitude to its linear dimensions, α_1 is greater than α_2 and σ is negative. The ratio α_2/α_1 may be obtained experimentally from the degree of depolarization in the scattering of light and from the Kerr effect.[10] Since γ is always positive, the two terms γ and σ are in general opposite in sign. For extremely elongated molecules, with a corresponding optical anisotropy, it is likely that σ predominates, causing a resultant negative deviation from the expanded Mosotti formula, Eq. (29). According to measurements of Danforth,[11] this appears to be true in the case of pentane. When $(\epsilon-1)v/3$, calculated from his measurements, is plotted as a function of density, all but the last point lie on a straight line (Fig. 1). Extrapolation to zero density yields a value of P_0 equal to 26.5 cc. The slope of the line deviates from P_0^2, the Mosotti value, by a factor of 0.95 leading to a value of -0.05 for $\gamma+\sigma$. Unfortunately, adequate data on the equation of state of pentane vapor and on the optical anisotropy of the pentane molecule are not available for the calculation of γ and σ. However, since γ has about the same value for all nonpolar molecules, a reasonable estimate is 0.15. With this value σ becomes about -0.20. From Eq. (37) the ratio α_2/α_1 is then estimated as about 0.5, a reasonable value for the optical anisotropy of the pentane molecule. It should also be remarked that the essential linearity of the experimental points in Fig. 1, confirms the adequacy of the expansions (27) and (34) even at liquid densities.

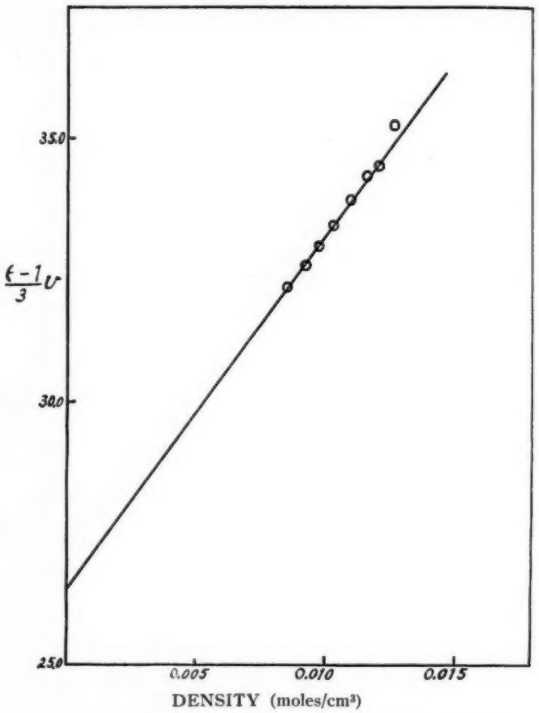

FIG. 1. Dielectric constant of liquid pentane as measured by Danforth.

[10] See Marx, *Handbuch der Radiologie*, Teil II; Debye and Sack, *Theorie der elektrischen Molekulareigenschaften;* Placzek, *Rayleigh-Streuung und Raman-Effekt.*

[11] Danforth, Phys. Rev. **38**, 1224 (1931).

Appendix

Outlines of the more important calculations, upon which the foregoing formulas are based will be presented here. Use is made of the generalized Green's theorem

$$\int^v \nabla \mathbf{F} = \int^A \mathbf{F} d\mathbf{A},$$

where the surface integral is extended over the boundaries of the volume v. The dyadic $\nabla\mathbf{F}$ may be written as follows

$$\nabla\mathbf{F} = \sum_{l,k=1}^{3} \mathbf{s}_l\mathbf{s}_k(\partial F_l/\partial x_k)$$

and the theorem may be proved by consideration of the components

$$\int^v \frac{\partial F_l}{\partial x_k} dv = \int^A F_l \mathbf{s}_k \cdot d\mathbf{A}$$

as for the usual Green's theorem. For brevity, we shall generally suppress the symbol **1** for the unit dyadic in what follows.

Calculation of $\bar{\mathbf{T}}_{ik}$:

From Eqs. (3) and (22), we may write after dropping subscripts, which are here superfluous

$$-\bar{\mathbf{T}}_{ik} = \frac{1}{v}\int^v \nabla\nabla(1/r)e^{-\beta W(r)}dv,$$

where $W(r)$ is the potential of the average force between a pair of spherical molecules and r is their separation. The integration is of course to be extended over the volume occupied by the dielectric. We may suppose that molecular repulsion, $W\to\infty$, causes the integrand to vanish in the neighborhood of $r=0$. Thus, the region within a sphere of arbitrarily small radius constructed about the origin can make no contribution to $\bar{\mathbf{T}}_{ik}$,

$$-\bar{\mathbf{T}}_{ik} = \frac{1}{v}\int_0^v \nabla\nabla(1/r)e^{-\beta W(r)}dv,$$

where the small sphere is excluded from the region of integration. Making use of the identity $e^{-\beta W} = 1+(e^{-\beta W}-1)$, we may now write

$$-\bar{\mathbf{T}}_{ik} = \frac{1}{v}\int_0^v \nabla\nabla\left(\frac{1}{r}\right)dv + \frac{1}{v}\int_0^\infty \nabla\nabla\left(\frac{1}{r}\right)(e^{-\beta W(r)}-1)dv.$$

The second integral can be extended over the whole of space, since the integrand, by virtue of the known properties of $W(r)$ will diminish asymptotically at least as rapidly as r^{-4}, and no significant contribution can arise from distant regions, outside the volume occupied by the dielectric. Transformation to polar coordinates and integration over angles shows immediately the second integral vanishes and we have

$$-\bar{\mathbf{T}}_{ik} = \frac{1}{v}\int_0^v \nabla\nabla(1/r)dv.$$

From this point on the calculation is formally identical with the classical one, the small sphere about the origin, playing the role of the Lorentz cavity. Transformation to a surface integral by means of Green's theorem yields

$$-\bar{\mathbf{T}}_{ik} = (1/v)\left\{\int^{A_e}\nabla(1/r)d\mathbf{A} - \int^{A_i}\nabla(1/r)d\mathbf{A}\right\},$$

where the first integral is taken over the exterior surface A_e, consisting of a pair of parallel planes, and the second integral over the interior surface A_i, consisting of the small sphere, all normals being outwardly directed. Evaluation of these integrals leads to Eq. (11).

Calculation of $\overline{\mathbf{T}_{ik}\cdot\mathbf{T}_{kl}}$:

Making use of Eq. (22), we may write

$$\overline{\mathbf{T}_{ik}\cdot\mathbf{T}_{kl}} = \frac{1}{v^2}\int^v\int \mathbf{T}_{ik}\cdot\mathbf{T}_{kl}e^{-\beta W_{ikl}}dv_k dv_l,$$

where W_{ikl} is the potential of the average force acting between the group of three molecules. In order to make the calculation feasible, we ignore attractive forces and assume the molecules to be rigid spheres of diameter a. For this case, we have

$$\overline{\mathbf{T}_{ik}\cdot\mathbf{T}_{kl}} = \frac{1}{v^2}\int_\omega^v\int \mathbf{T}_{ik}\cdot\mathbf{T}_{kl}dv_k dv_l,$$

where the integrations extend over the volume of the dielectric, excluding a region ω determined by two spheres of radius a, concentric with the molecules i and k. We first integrate over the configuration space of molecule l, transforming to surface integrals by means of Green's theorem.

$$\int \mathbf{T}_{ik}\cdot\mathbf{T}_{kl}dv_l = v\mathbf{T}_{ik}\cdot\bar{\mathbf{T}}_{kl} - \frac{4\pi a^3}{3}\mathbf{T}_{ik}^2 + \mathbf{T}_{ik}\cdot\mathbf{t}_{ik}$$

where $\bar{\mathbf{T}}_{kl}$ is given by Eq. (11) and

$$\mathbf{T}_{ik}\cdot\mathbf{t}_{ik} = 0 \qquad r_{ik} > 2a$$

$$= \frac{2\pi}{3r_{ik}^3}\left\{\left[-\frac{3}{8}\frac{r_{ik}}{a} + \frac{1}{16}\frac{r_{ik}^3}{a^3} + \frac{2a^3}{r_{ik}^3}\right] - \frac{3\mathbf{r}_{ik}\mathbf{r}_{ik}}{r_{ik}^2}\left[+\frac{3}{8}\frac{r_{ik}}{a} - \frac{1}{16}\frac{r_{ik}^3}{a^3} - \frac{2a^3}{r_{ik}^3}\right]\right\}$$

$$a \le r_{ik} < 2a.$$

The term $\mathbf{t}_{ik}$ arises from the overlapping of the spheres of exclusion for l about i and k when r_{ik} is less than $2a$, which decreases the interior surface over which the integration extends. Integration of the above expression over all configurations of k outside the sphere of exclusion round i yields

$$\overline{\mathbf{T}_{ik}\cdot\mathbf{T}_{kl}} = \bar{\mathbf{T}}_{ik}\cdot\bar{\mathbf{T}}_{kl} - 5\pi^2/3v^2,$$

the result given in Eq. (24), the symbol for the unit dyadic being suppressed.

Calculation of $\overline{\mathbf{T}_{ik}^2}$:

From Eqs. (3) and (22) we may write

$$\overline{\mathbf{T}_{ik}^2} = \frac{1}{v}\int^v \frac{1+3\mathbf{r}\mathbf{r}/r^2}{r^6}e^{-\beta W(r)}dv,$$

where r is the distance between the pair of molecules i and k, the subscripts being omitted here as superfluous. Since the potential of average force $W(r)$ is independent of the

angular coordinates, we get after integrating over them

$$\overline{\mathbf{T}_{ik}^2}=\frac{8\pi}{v}\int_0^\infty\frac{1}{r^4}e^{-\beta W(r)}dr,$$

the integration being taken over all of space instead of just the volume of the dielectric since the integrand diminishes sufficiently rapidly to make distant contributions entirely negligible. If attractive forces are neglected and the molecules are treated as hard spheres

$$W(r)=\infty \qquad 0\leq r<a$$
$$=0 \qquad r>a$$

we have

$$\overline{\mathbf{T}_{ik}^2}=\frac{8\pi}{3v}\frac{1}{a^3}=\frac{16\pi^2N}{9v}\frac{1}{b}$$
$$b=2\pi Na^3/3,$$

which is the result of Eq. (24). If attractive forces are not altogether neglected, but the dependence of $W(r)$ on density is ignored, we have

$$W(r)=\infty \qquad 0\leq r<a$$
$$=V(r) \qquad r>a$$

where $V(r)$ is the potential of the attractive van der Waals forces between an isolated pair of molecules. According to modern theory this potential has the form $-C/r^6$ where C is a constant. Expanding e^{+C/r^6kT} in series and neglecting terms of order $1/T^2$ and higher we obtain

$$\overline{\mathbf{T}_{ik}^2}=(16\pi^2N/9vb)(1+\tfrac{1}{3}NC/a^6RT).$$

However, from the theory of the equation of state, the van der Waals A constant is given by

$$A=-2\pi N^2\int_a^\infty V(r)r^2dr=\frac{2\pi N^2C}{3a^3},$$

so that we may write

$$NC/a^6=A/b$$

and we have

$$\overline{\mathbf{T}_{ik}^2}=(16\pi^2N/9bv)(1+A/3bRT),$$

leading to Eq. (28) for γ.

Calculation of $\overline{\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}}$ for Anisotropic Molecules:

Since $\boldsymbol{\alpha}^{(i)}\mathbf{T}_{ik}$ depends only on the coordinates of the centers of gravity of i and k and on the orientation of i alone, we may write with a slight generalization of Eq. (23)

$$\overline{\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}}=\frac{1}{8\pi^2v}\int d\omega_i\int^v\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}e^{-\beta\overline{W}}dv_k,$$

where $\overline{W}$ is the potential of the force acting between i and k averaged over all configurations of the other molecules and over the orientation of k. The above integral is extended over all positions of the center of gravity of k and over all orientations of i. Molecular repulsive forces will cause $e^{-\beta\overline{W}}$ to vanish in a region Ω containing the center of i and bounded by a surface A, fixed relative to a set of axes in i, for example the principal optical axes n_1, n_2, n_3. If we neglect attractive forces outside Ω, we may write

$$\int^v\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}e^{-\beta\overline{W}}dv_k=\int_\Omega^v\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}dv_k.$$

Making use of Green's theorem and Eq. (3) we may transform the above integral as follows

$$\int_\Omega^v\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}dv_k=-\int^{A_e}\boldsymbol{\alpha}^{(i)}\cdot\nabla\left(\frac{1}{r}\right)d\mathbf{A}+\int^{A_i}\boldsymbol{\alpha}^{(i)}\cdot\nabla\left(\frac{1}{r}\right)d\mathbf{A},$$

where r is the distance between i and k, and A_e is the exterior boundary consisting of two infinite parallel planes. Since A_e is independent of the orientation of molecule i, we may evaluate the first surface integral at once

$$-\int^{A_e}\boldsymbol{\alpha}^{(i)}\cdot\nabla\left(\frac{1}{r}\right)d\mathbf{A}=4\pi\boldsymbol{\alpha}^{(i)}\cdot\mathbf{s}_1\mathbf{s}_1.$$

The interior surface depends upon the orientation of i, but we may write

$$d\mathbf{A}_i=\sum_{l=1}^{3}\mathbf{n}_l(\mathbf{n}_l\cdot d\mathbf{A}_i),$$

where $\mathbf{n}_l\cdot d\mathbf{A}_i$ is independent of the orientation of i. Using Eq. (31), we obtain

$$\int_\Omega^v\boldsymbol{\alpha}^{(i)}\cdot\mathbf{T}_{ik}dv_k=4\pi\boldsymbol{\alpha}^{(i)}\cdot\mathbf{s}_1s_1-4\pi\sum_{l,s=1}^{3}\mathbf{n}_l\mathbf{n}_s\alpha_sJ_{ls},$$

$$J_{ls}=-\frac{1}{4\pi}\int^{A_i}\mathbf{n}_s\cdot\nabla\left(\frac{1}{r}\right)\mathbf{n}_l\cdot d\mathbf{A},$$

where J_{ls} is independent of the orientation of i. When the above expression is averaged over all orientations we obtain

$$\overline{\boldsymbol{\alpha}^{(i)}\mathbf{T}_{ik}}=\frac{1}{v}\left(4\pi\bar{\alpha}\mathbf{s}_1\mathbf{s}_1-\frac{4\pi}{3}\sum_{l=1}^{3}\alpha_lJ_{ll}\right),$$

which is identical with Eq. (33). This follows from the fact that

$$(1/8\pi^2)\int\mathbf{n}_l\mathbf{n}_sd\omega_1=\delta_{ls}/3.$$

The vector $\mathbf{n}_l$ may be expressed as

$$\mathbf{n}_l=\sum_{m=1}^{3}\mathbf{s}_m(\mathbf{n}_l\cdot\mathbf{s}_m),$$

where $\mathbf{s}_m$ is one of the set of mutually orthogonal unit vectors fixed relative to the external field and boundaries Thus an average of $\mathbf{n}_l\mathbf{n}_s$ over all orientations of the set of axes $\mathbf{n}_1$, $\mathbf{n}_2$, and $\mathbf{n}_3$ is

$$\overline{\mathbf{n}_l\mathbf{n}_s}=\sum_{m,\,m'=1}^{3}\mathbf{s}_m\mathbf{s}_{m'}\overline{(\mathbf{n}_l\cdot\mathbf{s}_m)(\mathbf{n}_s\cdot\mathbf{s}_{m'})}.$$

Since the average of the product of any pair of direction cosines, $(\mathbf{n}_l\cdot\mathbf{s}_m)(\mathbf{n}_s\cdot\mathbf{s}_{m'})$ which transform one set of orthogonal vectors into another, vanishes unless $l=s$ and $m'=m$, when it is $\frac{1}{3}$, and $\sum_{m=1}^{3}\mathbf{s}_m\mathbf{s}_m$ is equal to the unit dyadic.

Note Added in Proof:

Instead of expanding $(\epsilon-1)v/3$ in powers of α as we have done in Eq. (27), we may expand the Mosotti expression $(\epsilon-1)v/(\epsilon+2)$.

$$\frac{\epsilon-1}{\epsilon+2}v=\frac{P_0}{v}\left[1+\gamma\frac{P_0}{v}-\left(\frac{15}{16}+2\gamma\right)\left(\frac{P_0}{v}\right)^2+\cdots\right].$$

We note that when P_0/v is small, the fluctuations cause a

positive deviation from the Mosotti law. As the density is increased, this deviation becomes smaller, and vanishes when v is approximately equal to b or $2\pi Na^3/3$. The corresponding density is about twice ordinary liquid densities. This is reasonable, for one might expect translational fluctuations to become relatively unimportant not only in solids but also in liquids. Not much significance is to be attached to the value $v=b$ predicted by the above formula since it is probably necessary to take terms of higher order in P_0/v into account as liquid densities are approached. It should be emphasized, however, that although the Mosotti value of $(\epsilon-1)v/(\epsilon+2)$ is approached at some particular density, the Mosotti formula cannot give the correct variation of ϵ with density. This consideration may at first sight seem to make the application of our equations to liquid pentane seem questionable. However, we must remember that although the translational fluctuation may become small at liquid densities, this is not true of the rotational fluctuation. It might, therefore, be better to suppose that the γ contribution to the slope vanishes and that only σ is important. The value of σ in liquid pentane would then be -0.05, with a ratio of 0.86 instead of 0.5. It is apparent that we can attach only qualitative significance to these figures.

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Thermal Transitions in Copper Sulphate Pentahydrate Molecular Rotation and the Dehydration of Hydrates

T. IVAN TAYLOR* AND HAROLD P. KLUG, *University of Idaho, Moscow, Idaho*

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A study of the thermal transitions in copper sulphate pentahydrate has been made from warming curves obtained by a differential thermocouple method. Small transitions were observed at 29°C, 35°C, 53.7°C, and dehydrations at 96.5°C, 102°C, and at 113°C. The first three of these may be interpreted as transitions from oscillation to rotation of the water molecules in the crystal. The last three are associated with the stepwise dehydration to the tetra-, tri-, and monohydrates, respectively. The existence of the tetrahydrate, not previously known, has been demonstrated. A discussion of the dehydration in the light of its crystal structure is given. A mechanism of dehydration by heat, based on the concept of molecular rotation, has been suggested.

SINCE Pauling's explanation[1] of certain observed transitions in solids on the basis of a gradual transition from oscillational motion of the molecules about equilibrium positions to complete rotation, the phenomenon has proved to be of rather wide occurrence in accordance with his prediction. In many substances the excitation of rotation of the molecules or groups is accompanied by gradual and sometimes sharp changes in such properties as dielectric constant, heat capacity, specific volume, coherent scattering of x-rays, and crystal structure. Pohlman[2] has studied the adsorption spectra of a number of ammonium salts in the neighborhood of the transition temperatures. Shearin[3] has also recently found that there is an infrared absorption at wave-lengths of about 3.7μ for solid hydrogen chloride which indicates hindered rotation. This observation is in contrast to the results of Errera and Sack[4] working with Hertzian waves. Evidence that molecular rotation in certain organic crystals is initiated simultaneously with atomic vibrations has been given by White and Morgan[5] and Yager and Morgan.[6]

As is shown by x-ray studies of the transitions observed in certain crystals, for example, sodium nitrate,[7] ammonium nitrate,[8] and *n*-amyl ammonium chloride,[9] rotation of the molecules or groups may or may not be initiated at a polymorphic inversion. If the transition is accompanied by a change in crystal structure, the con-

* Now at Columbia University, New York City.

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[2] Pohlman, Zeits. f. Physik **79**, 394 (1932).
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version may be rather abrupt though not necessarily discontinuous. This behavior is shown by such solids as hydrogen chloride,[10] nitrogen,[11] sodium cyanide,[12] and others.[13] With other crystals such as sodium nitrate or *n*-amyl ammonium chloride the transition is more gradual without a definite change in crystal structure. The definiteness of all these transitions is generally explained by assuming a cooperative phenomenon in which it is supposed that as soon as a molecule changes from the oscillatory state to the rotational state its whole surroundings will be involved and the other molecules will follow immediately. The resulting changes in lattice or molecular forces often result in a change in crystal structure.

In Pauling's theoretical treatment of a simple diatomic molecule, he considered the molecule bound like a harmonic oscillator in the crystal fields. The potential function representing the averaged interaction of the molecule with its surrounding molecules is given in its simplest form by

$$V = V_0(1-\cos 2\theta),$$

in which V_0 is a constant obtainable from specific heat data and θ is the angle made by the figure axis of the molecule with some fixed direction. The transition from oscillation to rotation is assumed to start when the kinetic energy of the molecules becomes of the order of magnitude of $2\ V_0$ or at a temperature of $T=2V_0/k$ when rotation weakens the binding forces. Thus the binding force is found to depend upon the temperature. For lower temperatures the molecules oscillate about $\theta=0$, while above the transition they rotate, being hindered in their motion by the crystal fields.

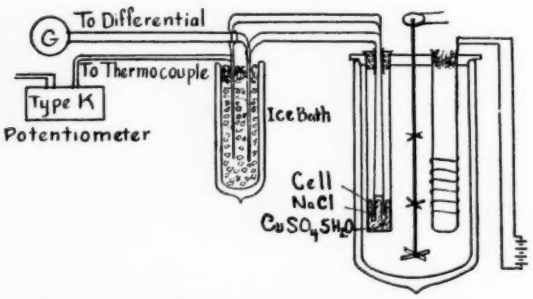

FIG. 1. Apparatus for heating and cooling curves.

Since Pauling's work, a number of more complete mathematical treatments of wider application have been given. Some of these consider molecules of different three-dimensional configurations; others try to represent more fully the magnitude of the crystal fields and their effects on dielectric constant and specific heat. Of these the work of Stern,[14] Nielson,[15] Frenkel and his co-workers,[16] Fowler,[17] and Devonshire,[18] may be mentioned.

The purpose of this paper is to study the dehydration of copper sulphate pentahydrate and to show that transitions occur which may be interpreted as transitions from oscillation to rotation of the water molecules. Since the crystal structure of this hydrate has recently been determined[19] it lends itself to a rather complete analysis. A theory of dehydration on the basis of molecular rotation of the water molecules in certain salt hydrates as mentioned by one of us recently[20] is suggested and may be extended after further data are available. It seems possible at the present time that the vapor pressure of certain hydrates may be related to the statistical probability of the molecules acquiring enough vibrational-rotational energy to break away from the crystal lattice.

EXPERIMENTAL

A thermal analysis of copper sulphate from -75°C to 160°C was made by taking the heating curves with differential thermocouples. A diagrammatic illustration of the apparatus is given in Fig. 1. Double silk covered copper (B. S. No. 40) and constantan (B. S. No. 30) wire were used for both the differential and the temperature thermocouples. Calibration curves were obtained from the melting point curves of the following carefully purified substances: chloroform, monochlorbenzene, carbon tetrachloride; ice point; and sodium sulphate decahydrate, naphthalene,

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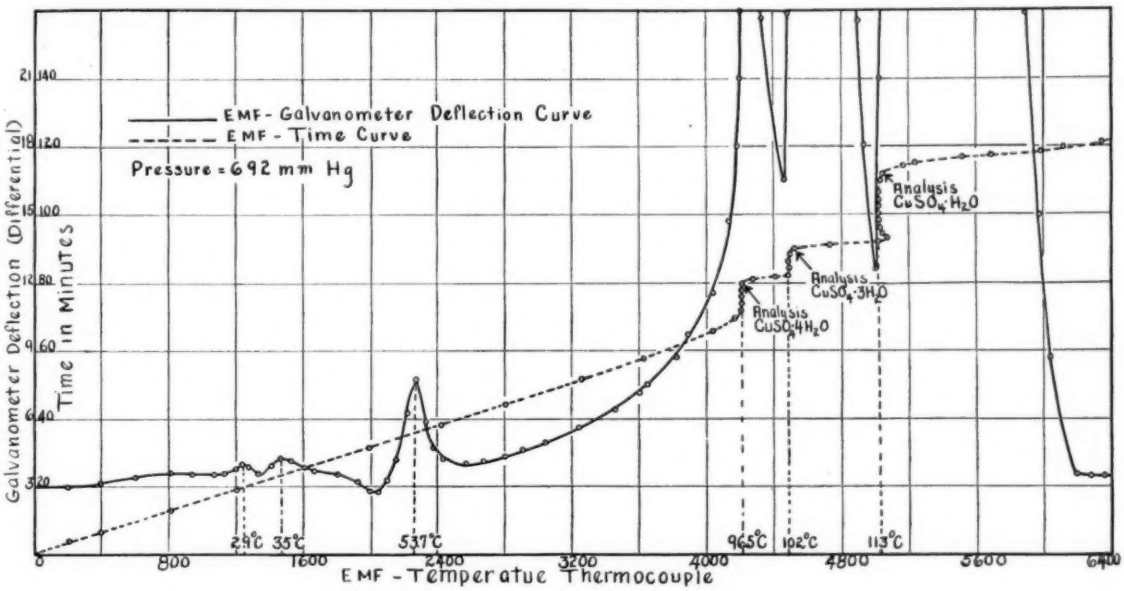

FIG. 2. Heating curves for copper sulphate pentahydrate.

benzoic acid, and salicylic acid. Different bath liquids were used according to the temperature range.[21] Over the transition ranges three different bath liquids were used to eliminate any uncertainties which might arise due to the possibility of transitions in them.

The cell was made by drilling two holes in a copper block and fitting them with thin-walled glass tubes. One tube was filled with about 1.5 g of copper sulphate pentahydrate and the other with an equal quantity of sodium chloride. Sodium chloride was chosen as a blank to run against copper sulphate because it has nearly the same specific heat and is known to have no transitions over the temperatures range studied.

A Leeds and Northrup type R−2500 C galvanometer with a sensitivity of 1.6 microvolts per mm was connected directly to the differential thermocouple. The scale was placed at about 75 cm from the galvonometer, so that one centimeter deflection corresponds to about one-third degree. The e.m.f. of the temperature thermocouple was read to the nearest 2 microvolts by means of a Leeds and Northrup type K potentiometer in conjunction with a type HS galvanometer (L. and N., year 1913).

In making a run the bath was cooled with solid carbon dioxide and then heated at a constant rate. Readings of the temperature thermocouple and the galvanometer deflection were taken every minute, or every half minute in the neighborhood of a transition. Twenty-five to thirty runs were made over different temperature ranges. Some were made using different rates of heating, varying from 2°C per minute to 0.5°C per minute. Other runs were made in which the particle size of the copper sulphate was varied. Most runs were made at pressure of about 690 mm of mercury,[22] but a few runs were made under partial vacuum (5 cm Hg). The higher rates of heating give larger changes in galvanometer deflections, but there is a loss in detail and accuracy of temperature readings. Large particles do not give as sharp breaks in the latter part of the time temperature curves because the second stage of the dehydration probably starts before the first has reached to the center of the particle. On the other hand, too small particles prevent escape of liberated water vapor from the center of the sample. The most favorable conditions seemed to be a rate of heating of from 1°C to 1.5°C per minute and a particle size of $>100<150$ mesh (about 0.09 mm).

The curves for the temperature range −75°

[21] *International Critical Tables*, Vol. I, p. 61.

[22] The average atmospheric pressure at Moscow, Ida., is about 690 mm of mercury.

to 10°C are not reproduced because there was no abnormal deflection of the galvanometer and the temperature rose at a constant rate. Curves showing typical behavior above these temperatures are given in Fig. 2, which gives the results over the range 10°C at 160°C obtained by use of a two junction differential thermocouple. The analyses represented on Fig. 2 were obtained by stopping different runs at the points indicated and analyzing for both copper and water remaining. The results of the analyses for different runs did not vary more than 0.20 percent from the theoretical values calculated from the formulae $CuSO_4 \cdot 4H_2O$, $CuSO_4 \cdot 3H_2O$ and $CuSO_4 \cdot H_2O$. The value of 2270 microvolts for the higher of the small maxima could be reproduced under the same conditions on the same or different samples to within 5 to 10 microvolts using the same differential. The smaller maxima at about 1220 microvolts and 1470 microvolts were not so reproducible, different runs varying from 5 to 50 microvolts. This larger variation may be due in part to the smallness of the changes and the comparatively high rate of heating. It was found difficult to reproduce these smaller maxima later using different differentials with heavier wire, or with too much insulation. Instead of rising to a maximum there was simply a definite change in the slope of the differential curve at 50° to 55°C. The changes corresponding to the dehydrations shown, however, were always obtained.

Discussion of the Warming Curves

As the temperature of the cell containing the sodium chloride and the copper sulphate was raised there should have been no abnormal deflection of the galvanometer connected to the differential thermocouple unless there is a fairly sudden change in the heat capacity or heat adsorption of the copper sulphate. Apparently there is such a change at about 29°C, 35°C and especially at 53.7°C. Greater sensitivity probably would reveal further detail in regard to the lower transitions. In the light of previous work on the rotation of molecules in solids, these changes may be interpreted as changes from oscillation to rotation of the water molecules. This is in accord with the suggestion of Pauling[1] that the water molecules in potassium alum must be rotating at room temperatures in order to explain certain x-ray data showing high crystallographic symmetry. The rotation of the water molecules in some complex cyanide hydrates was also suggested by Errera and Sack[4] to explain some sharp changes in dielectric constants. Further, Fowler's treatment[17] of the dielectric constant of Rochelle salt assumes rotation of the water molecules. A transition in copper sulphate in the neighborhood of 50°–55°C has been observed by a number of investigators by measurement of conductivity, electromotive force, solubility and dilation. These have been summarized by Abraham and Lucasse.[23]

The three small transitions observed may possibly be due to rotation of all the water molecules about the three crystallographic axes following Fowler's treatment[17] of Rochelle salt, but it seems possible in this case that the ones at 29°C and 35°C are due to initiation of rotation of the two water molecules which first come off to give the trihydrate and the one at 53.7°C to the next two occurring together. Since the effects observed here are small, much smaller than similar ones for ammonium chloride for example, the rotations seem to be associated with a particular axis rather than end for end or free rotation. A few runs at slightly higher pressures where thermal changes were not masked by the high rate of dehydration indicated the possibility of a change to free rotation at or just below the temperature of spontaneous decomposition. This point requires further investigation. Similar transitions were observed in a number of other hydrates as well as in the heavy water hydrates of copper sulphate. At present it appears that in certain hydrates such as sodium sulphate decahydrate there is a complete breakdown and dehydration at the initiation of rotation giving a solution of the salt in its water of crystallization.

On heating the sample of copper sulphate above the 53.7°C transition at a pressure of 692 mm of mercury,[22] the rate of dehydration gradually increases up to 96.5°C where dehydration continues at a constant temperature until one molecule of water is lost leaving a residue of $CuSO_4 \cdot 4H_2O$. Then at 102°C the second molecule of water comes off until the composition is $CuSO_4 \cdot 3H_2O$. At 113°C two more molecules of

[23] Abraham and Lucasse, J. Phys. Chem. **37**, 521 (1933).

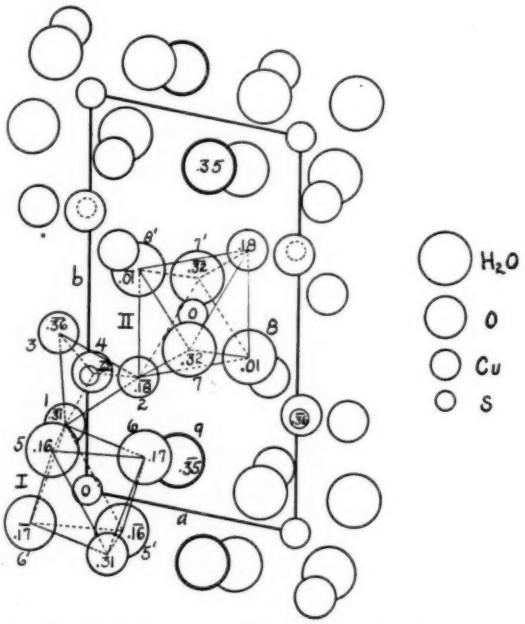

FIG. 3. Projection of the $CuSO_4 \cdot 5H_2O$ structure on a plane normal to the c axis. Examples of the coordination octahedra around the copper atoms, and the SO_4 tetrahedra are shown. Noncoordinated water molecules are drawn heavier. The numbers outside the circles correspond with the numbering of the various atoms by Beevers and Lipson. The numbers inside the circles are the z parameters.

water come off together at a constant temperature. In these experiments the fifth one was not lost at a definite temperature but only gradually with increased temperature. The heat change in these processes corresponds roughly to the heat of efflorescence, that is, the heat of hydration plus the heat of vaporization whereas the heat change in the case of those hydrates melting in their water of crystallization corresponds roughly to the heat of hydration. When a sample was run at a pressure of 5 cm of mercury, the copper sulphate dehydrated at a constant temperature of 55°C without any indication of a stepwise dehydration.

The results definitely indicate the existence of a tetrahydrate of copper sulphate and they have been reproduced as many as twenty times. This finding is difficult to interpret in view of the large amount of data on the vapor pressure of copper sulphate showing the existence of only the 5, 3, and 1 hydrates even up to fairly high temperatures.[24] A possible explanation lies in the assumption that the vapor pressure curve

[21] Carpenter and Jette, J. Am. Chem. Soc. **45**, 578 (1923).

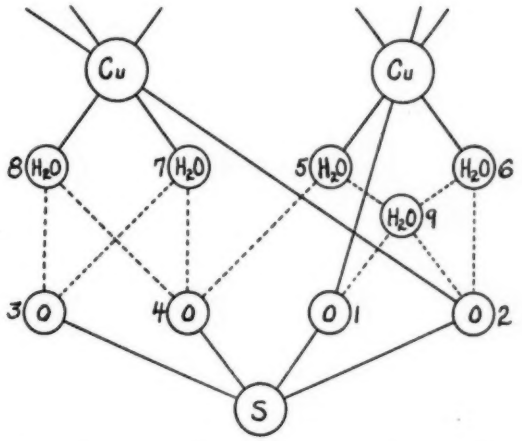

Fig. 4. Schematic diagram of the arrangement of bonds in $CuSO_4 \cdot 5H_2O$. Hydrogen bonds are represented by dashed lines, other bonds by solid lines. The SO_4 oxygens do not all belong to the same SO_4 group.

of the pair $CuSO_4 \cdot 5H_2O - CuSO_4 \cdot 4H_2O$ crosses the vapor pressure curve of $CuSO_4 \cdot 4H_2O - CuSO_4 \cdot 3H_2O$ at the higher temperatures. The vapor pressure of the $CuSO_4 \cdot 5H_2O - CuSO_4 \cdot 3H_2O$ pair would then be higher at lower temperatures where most of the measurements have been made. It is also not unreasonable in view of the structure relations of copper sulphate that at lower temperatures the vapor pressure of the pair $CuSO_4 \cdot 5H_2O - CuSO_4 \cdot 4H_2O$ may be very nearly the same as the pair $CuSO_4 \cdot 4H_2O - CuSO_4 \cdot 3H_2O$, the difference becoming significantly greater only at higher temperatures. We can say, however, that at 97°C and a pressure of 692 mm of mercury,[22] the vapor pressure of the pair $CuSO_4 \cdot 5H_2O - CuSO_4 \cdot 4H_2O$ is higher and that the tetrahydrate does exist, though possibly unstable. The definiteness of the temperature of dehydration and the analyses show that the observed curves are not due to any type of mixture of the five and three hydrate but to a definite compound.

CRYSTAL STRUCTURE OF $CuSO_4 \cdot 5H_2O$ AND ITS DEHYDRATION

Beevers and Lipson[19] have recently made a rather complete determination of the crystal structure of copper sulphate pentahydrate. The crystal is triclinic and contains two molecules to the unit cell. The copper atoms lie on centers of symmetry at (000) and $(\frac{1}{2}\frac{1}{2}0)$ and the other atoms are in the general positions $\pm(xyz)$ of the space

group C_i^1 with the parameters of the sulphur atoms being (0.01, 0.29, and 0.64). Each copper atom is surrounded by a slightly distorted octahedron consisting of four water molecules in an approximate plane and two oxygens from the sulphate groups. The odd water molecule touches two oxygens of different sulphate groups and two waters of a copper octahedron. It is apparently bound very firmly with a tetrahedral arrangement of bonds while the other waters have only a coplanar system of three bonds. A projection of the atomic arrangement in the unit cell, and a schematic diagram of the bond structure are shown in Figs. 3 and 4.

Beevers and Lipson have attempted to explain the dehydration of copper sulphate pentahydrate to the trihydrate by assuming that the water molecules first break up around the copper at (000) due to the greater instability of the distorted coplanar arrangement of bonds, and then around the copper at $(\frac{1}{2}\frac{1}{2}0)$ giving the monohydrate. In the light of the results of this paper their explanation is hardly complete. In fact their structure determination seems to be in even better agreement with our results and conclusions.

Dehydration will occur when the thermal agitation of the water molecules becomes great enough to break the binding forces holding them in the lattice. This thermal agitation will be mostly distributed between vibrational and rotational motion. The increase in rotational motion with temperature contributes to the weakening of the binding forces. The strength of these bonds will depend upon their nature, the interatomic distances, and the amount of bond distortion in their formation. The four water molecules in the coordination octahedra are bonded to the copper atom by covalent square bonds.[25] Harker[26] has shown the square covalent radius of copper to be 1.32A. The covalent Cu−0 distance should then be 1.98A. In Table I the interatomic distances (Cu−5), (Cu−6), and (Cu−8) are seen to be in excellent agreement with this value. The other Cu−0 distance (Cu−7) is of the same type, its appreciably greater value indicating a weaker bond than the other three cases. The bonds from the copper atom to the sulphate oxygens in the octahedra are electrostatic in type. The water molecules of the coordination octahedra, as well as the fifth water molecule, probably form hydrogen bonds with oxygen atoms of the sulphate groups, the oxygen atoms of the octahedra, and the oxygen of the fifth water molecule (Fig. 4). No water molecule, however, forms a hydrogen bond with the oxygen atoms of its own octahedron. The hydrogen bond is an electrostatic or ionic type of bond,[27] and in the case of such bonds involving water molecules the hydrogen is much closer to the one oxygen than the other. Pauling[28] has shown that in ice these distances are 0.95A and 1.81A, respectively. The former is the normal electron-pair bond distance while the longer distance constitutes the ionic or electrostatic part of the hydrogen bond. Such bonds have been reported in the following hydrates, $Li_2SO_4 \cdot H_2O$[29] and $H_2C_2O_4 \cdot 2H_2O$.[30]

The strength of the hydrogen bond will depend, as in the case of any ionic bond, on the interatomic distance, becoming weaker as the bond distance becomes longer. It will also depend on the positions of the oxygen atoms involved, being more stable when the O−H :Ö: H−O angle approximates 105°, the angle found in the gaseous water molecule, and less stable as this angle suffers greater and greater distortion.

By means of the complicated trigonometrical formulas for distances within a triclinic cell, the interatomic distances listed in Table I have been calculated from the parameters given by Beevers and Lipson.[19]

The transitions observed at 96.5°C and 102°C correspond with dehydration to the tetrahydrate

TABLE I. *Interatomic Distances in the Unit Cell of* $CuSO_4 \cdot 5H_2O$.

Octahedon No. I	(Cu−1)* = 2.32A	(6−1) = 3.18A	(5′−1) = 3.18A
(Octahedron about	(Cu−5) = 1.97	(5−1) = 2.92	(6−5) = 2.75
Cu at 000)	(Cu−6) = 1.97	(6′−1) = 2.86	(6′−5) = 2.85
Octahedron No. II	(Cu−7) = 2.08	(8−2) = 3.06	(7−2′) = 3.25
Octahedron about	(Cu−8) = 1.95	(8−2′) = 3.19	(8−7) = 2.85
Cu at $\frac{1}{2}\frac{1}{2}0$)	(Cu−2) = 2.44	(7−2) = 3.12	(8−7′) = 2.80
Distances between	(8−3) = 2.58	(5−4) = 2.71	(6−2) = 2.78
oxygens of water	(8−4) = 2.66	(5′−9) = 2.71	(9−1) = 2.71
molecules and sul-	(7−4) = 2.58	(6−9) = 2.74	(9−2) = 2.96
phate groups	(7−3) = 2.90		

* These numbers correspond to the numbers given to the oxygen atoms in the cell by Beevers and Lipson:[19] see Fig. 3.

[25] We are indebted to Professor Linus Pauling for this suggestion.

[26] Harker, Zeits. f. Krist. **93**, 136 (1936).

[27] Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[28] Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).

[29] Zeigler, Zeits. f. Krist. **89**, 456 (1934).

[30] Zachariasen, Zeits. f. Krist. **89**, 442 (1934).

and thence to the trihydrate. That they are associated with the break up of the II octahedran rather than the I octahedron as postulated by Beevers and Lipson is evident from the following. It has been noted in II that water molecules (7) and (7′) are bonded to the copper by much weaker bonds than water molecules (8) and (8′), the interatomic distances being 2.08A and 1.95A, respectively. Furthermore the hydrogen bond between the water molecule (7) and sulphate oxygen atom (4) is very weak as evidenced by the interatomic distance of 2.90A. The other hydrogen bond distances (7−3), (8−4), and (8−3) are somewhat stronger, the interatomic distances being 2.58A, 2.66A, and 2.58A, respectively. In fact from a consideration of the bond strengths as based on the interatomic distances throughout the crystal it is seen that water molecules (7) and (7′) are the most loosely bound water molecules in the cell. Bond distortion likewise further contributes to the weakness of binding of these molecules. Beevers and Lipson have found the angle between oxygen atoms (3−7−4) to be 122° while that between oxygen atoms (3−8−4) is 108°. Hence water molecules (7) and (7′) would be expected to start rotating at lower temperature than any of the rest of the water molecules in the cell. It seems possible, therefore, to interpret the small transition at 29°C as the point at which they start rotating. Once two of the water molecules of the II octahedron are set to rotating the other two would be expected to do likewise soon, as a result of the disturbed equilibrium among the binding forces. The transition at 35°C is, thus, expected and is interpreted as the point where water molecules (8) and (8′) start rotating. This is in line with the dehydration to the trihydrate with the loss of molecules (8) and (8′) following that of (7) and (7′) at 96.5°C very closely, namely at 102°C provided the loss of the first two molecules does not materially affect the structure so as to change the binding of the next two in the unit cell.

Assuming that the breaking up of the first octahedron (II) to give the trihydrate does not materially affect the binding forces of the water molecules in the next octahedron (I), the transition at 53.7°C may be associated with the dehydration of the trihydrate at 115°C to give the monohydrate. This stage of the dehydration is, we believe, associated with the break up of the I octahedron instead of the II octahedron as postulated by Beevers and Lipson. From interatomic distances (Table I) the bond strengths for the four water molecules (5), (5′), (6), and (6′) are seen to be almost the same. They would therefore be expected to all start rotating at once and to all come off at once in dehydration. Bond distortion of the hydrogen bonds here contributes to the weakening of the bonds about equally for all four water molecules. The angles between oxygen atoms (9′−5−4) and (2−6−9) are 122° and 129° respectively. That this distortion does not result in the I octahedron breaking up first is probably to be attributed to the stabler bond arrangement due to the practically equal Cu−0 distances for the water molecules in the I octahedron.

Concerning the fifth water molecule it is evident that its original tetrahedral bonding arrangement should be quite stable, and that it would hardly be expected to start rotating until after the water molecules of the I octahedron have done so. From its dehydration behavior one would be led to believe that possibly after the break up of the I octahedron it becomes more firmly bound to the sulphate groups or that it becomes bound into the lattice by new bonds. Data are lacking for any further consideration of it at this time.

The results of this paper showing the new stage in the dehydration of copper sulphate pentahydrate do not necessarily mean that any of the previous work has been in error. It may simply mean that the difference between $CuSO_4 \cdot 4H_2O$ and $CuSO_2 \cdot 3H_2O$ becomes significantly great only at higher pressures and at temperatures higher than those ordinarily used (about 50°C). This deserves further study.

The authors gratefully acknowledge the valuable assistance of Professor Linus Pauling of the California Institute of Technology in the discussion of the bonding in the crystal. We also wish to express our sincere thanks to Dr. James A. Cooley of the Mathematics Department of this University for his valuable suggestions in connection with the interatomic distance calculations and to Professor J. J. Beaver of Columbia University for his advice and helpful discussions on the vapor pressure relations of the copper sulphate hydrates.

Studies on the Decomposition of Azomethane

III. Effect of Various Inert Gases [1]

DARRELL V. SICKMAN[2a] AND O. K. RICE,[2b] *Chemical Laboratory, Harvard University*

(Received June 1, 1936)

Data are presented on the decomposition of azomethane in the presence of several inert gases, relative activation efficiencies being given in Table II. The low efficiency of helium as compared to the other gases is taken as indicating that exchange of vibrational energy between molecules is more probable than the transition of translational into vibrational energy. The results are compared with other pertinent data, and the probable mechanism of energy exchange is discussed. Finally, some preliminary data on the effect of azomethane on reactive gases are given.

IN Part II[3] of this series of papers we presented data on the decomposition of azomethane in the presence of helium and calculated the relative activating efficiency of helium as compared to azomethane itself. In this paper we shall present and discuss data showing the effects of various other inert gases.

§1. EXPERIMENTAL DETAILS

The apparatus used was that described in Part I,[4] and the manipulations and general technique were the same as previously used. The various materials used were prepared as follows:

Deuterium, stated to be better than 99.5 percent pure, was kindly furnished by Professor Taylor of the Princeton Laboratory.

Nitrogen was taken from a tank, passed over hot copper, hot copper oxide, through alkaline pyrogallol, through a trap cooled in dry ice, and over fused potassium hydroxide.

Methane was prepared by the hydrolysis of methyl magnesium iodide in dibutyl ether solution, passed through two traps cooled by dry ice, bubbled through more methyl magnesium iodide in dibutyl ether solution, passed through another dry ice trap, condensed in a liquid air trap, pumped off, and distilled, the middle fraction being used.

Carbon monoxide was made by dropping 85 percent C.P. formic acid into concentrated sulfuric acid (both having been pumped off beforehand to remove other gases). It was then passed through two traps cooled by dry ice, through a wash bottle of alkaline pyrogallol, and through a third dry ice trap. About eight liters were run through the train before the sample used was collected.

Carbon dioxide was made by heating an evacuated vessel containing pure sodium bicarbonate. The gas was passed through two dry ice traps, condensed by means of liquid air, and distilled from dry ice to liquid air.

Mixtures of azomethane (prepared as in Part II) with the various inert gases were made in one of two ways. In the first method the azomethane was admitted to the storage bulb at a known pressure, condensed in a liquid air trap, the inert gas admitted and its pressure measured, and the azomethane then allowed to evaporate into the bulb. Such a mixture was allowed to stand overnight before using. In the second method the inert gas was admitted without condensing the azomethane and the total pressure measured. Such a mixture, having been well stirred in the process of making it, was sometimes used after a lapse of two hours. This would perhaps not allow sufficient time for complete mixing throughout all the connecting tubing, but the volume of the latter was negligibly small.

Generally when the gas was admitted from the storage bulb into the reaction vessel, equilibrium between them (requiring only 15–20 seconds) was allowed to become established and the initial pressure taken as the remaining pressure in the storage flask. In the case of a few runs made with water vapor as an inert gas, it being impractical to use large pressures, it was considered more accurate to calculate the initial pressures in the second and third runs made from the measured pressure for the first run and the known pressure distribution ratio between the reaction vessel and the storage flask. This pressure ratio served as a check on the initial pressure in the other cases. A few bad runs are connected with an error in the initial pressure reading, but as the source of this error was not known these runs are presented with the others, though they are not generally used in making up averages.

Mr. A. K. Solomon informs us that he has observed slow decomposition of azomethane in diffuse light, but we found no systematic changes in our results from allowing a mixture to stand in the storage bulb for a day, and we believe errors due to this cause are negligible.

§2. THE EXPERIMENTAL RESULTS

The initial rate of decomposition of azomethane in the inert gas mixtures was calculated from the rate of pressure increase and corrected for the external volume as in Part II. The relative activating efficiency, α, of the inert gas compared

[1] Presented at the San Francisco meeting of the American Chemical Society, August, 1935.

[2] Present addresses: (a) Columbia University; (b) University of North Carolina, Chapel Hill.

[3] J. Chem. Phys. **4**, 242 (1936).

[4] J. Chem. Phys. **4**, 239 (1936).

to azomethane at the same pressure was also obtained as before, using the curves of Fig. 1 of Part II to obtain the rate of decomposition of pure azomethane. The results are given in Table I, and some of them are also presented graphically in Figs. 1 and 2. In Table II we summarize the average values of α, including that for helium, and we also give the values, α', of the relative activating efficiency *per collision*, referred to azomethane as unity. From the formulas for the number of collisions between activated azomethane molecules and other molecules it may readily be seen that

$$\alpha' = \alpha[2M/(M+M_0)]^{\frac{1}{2}}[2\sigma_0/(\sigma+\sigma_0)]^2, \quad (1)$$

where M and M_0 are the molecular weights of the inert gas and azomethane, respectively, and σ and σ_0 are their respective kinetic theory radii (relative values only). Most of these values were taken from Binkele;[5] the value for azomethane was assumed to be the same as that of propane.[6] For deuterium the value for hydrogen was used. The values used are given in Table II.

TABLE I. *Summary of results.* (P_i = *initial azomethane pressure in mm,* P_{D_2} = *deuterium pressure, etc.;* K = *initial rate constant in sec.*$^{-1}$.)

Run	Log P_i	Log ($K\times10^5$)	α
	P_{D_2}/P_i = 5.00; 310°C		
126	0.929	1.755	0.67
127	.607	1.671	.71
128	.291	1.550	.62
129	$\bar{.}$069	1.107	
130	$\bar{1}$.718	1.339	.65
	P_{D_2}/P_i = 9.95; 310°C		
141	0.710	1.808	1.06
142	.393	1.700	0.83
143	$\bar{.}$076	1.582	.74
144	$\bar{1}$.757	1.438	.59
	P_{D_2}/P_i = 6.00; 290.4°C		
145	0.925	1.135	0.51
146	.600	1.081	.75
147	$\bar{.}$277	0.974	.65
148	$\bar{1}$.955	.873	.70
149	$\bar{1}$.633	.658	.35
	P_{D_2}/P_i = 3.02; 290.4°C		
150	0.858	1.105	0.88
151	$\bar{.}$537	0.953	.45
153	$\bar{1}$.891	.712	.44
	P_{N_2}/P_i = 5.04; 310°C		
171	0.977	1.671	0.19
172	.659	1.568	.20
173	.342	1.455	.19
174	.093	1.234	
175	$\bar{1}$.761	1.043	
	P_{N_2}/P_i = 5.05; 310°C		
176	0.973	1.705	0.30
177	.656	1.580	.23
179	$\bar{.}$028	1.348	.23
180	$\bar{1}$.714	1.154	.13
	P_{N_2}/P_i = 9.99; 310°C		
181	0.748	1.663	0.21
182	.430	1.538	.18
183	$\bar{.}$113	1.418	.17
184	$\bar{1}$.797	1.261	.13
185	$\bar{1}$.484	1.105	.12
	P_{CH_4}/P_i = 4.98; 310°C		
186	0.995	1.678	0.19
187	.676	1.590	.24
188	.357	1.485	.26
189	$\bar{.}$043	1.359	0.25
190	$\bar{1}$.727	1.205	.20
191	$\bar{1}$.415	1.165	.49
	P_{CH_4}/P_i = 10.01; 310°C		
192	0.691	1.662	0.25
193	.372	1.547	.23
194	$\bar{.}$055	1.435	.24
195	$\bar{1}$.736	1.306	.24
196	$\bar{1}$.420	1.163	.24
	P_{CO}/P_i = 5.01; 310°C		
250	0.984	1.628	0.08
251	.664	1.537	.12
252	.343	1.428	.13
253	.025	1.292	.13
254	$\bar{1}$.713	1.128	.09
	P_{CO}/P_i = 10.00; 310°C		
255	0.735	1.625	0.14
256	.413	1.497	.12
257	$\bar{.}$095	1.389	.13
258	$\bar{1}$.777	1.257	.14
	P_{CO_2}/P_i = 5.03; 310°C		
301	0.992	1.667	0.16
302	.670	1.574	.20
303	.347	1.461	.20
304	$\bar{.}$029	1.350	.24
305	$\bar{1}$.711	1.199	.21
306	$\bar{1}$.400	1.055	.23
	P_{CO_2}/P_i = 9.95; 310°C		
307	0.718	1.626	0.16
308	.396	1.541	.20
309	$\bar{.}$077	1.433	.22
310	$\bar{1}$.759	1.304	.22
311	$\bar{1}$.442	1.151	.20
	P_{CO_2}/P_i = 50.0; 310°C		
312	0.066	1.600	0.17
313	$\bar{1}$.746	1.507	.20
314	$\bar{1}$.426	1.376	.18
	P_{H_2O}/P_i = 0.98· 310°C		
315	0.704	1.528	0.38
316	.387	1.418	.44
317	.068	1.282	.41

TABLE II. *Relative activation efficiencies.*

Substance	σ	α	α'
Azomethane	1.76	1.00	1.00
N_2	1.23	0.19	0.21
CO	1.24	.12	.13
CH_4	1.33	.23	.20
H_2O	1.00	.41	.46
CO_2	1.28	.20	.25
D_2	1.07	.66	.37
He	1.00	.12	.07

A few experiments on the effect of nitrogen on the azomethane decomposition have been made by Ramsperger.[7] His value of α is in good agreement with ours, though the significance of this may be doubted in view of the difference between his results and ours on pure azomethane.

Table I contains all runs made with the inert gases listed except one with deuterium (No. 152) in which there was a marked variation in rate during the run and one with nitrogen (No. 178) which was known to be spoiled. In a few cases in which some gross error must have been made α was not calculated, nor were the results included in Fig. 1 or 2. No. 191 was not included in calculating the average for methane. The run numbers may be correlated with those given in Part II. Runs not appearing in either paper represent runs made in the presence of gases which were not inert (see §4, below).

§3. Discussion of the Results

In all cases considered here the values of α for any given gas are the same within the experimental error over the range of conditions studied. The most erratic results occurred with deuterium, but even in this case Fig. 1 indicates that while there is some scattering of the points there appears to be no appreciable trend away from that predicted for an inert gas. This is, indeed, rather remarkable in this particular case, for we found, in a series of experiments which will be reported later, that the apparent value of α shows marked trends with pressure and

[5] Binkele, Ann. d. Physik **15**, 729 (1932).
[6] Melaven and Mack, J. Am. Chem. Soc. **54**, 899 (1932).
[7] Ramsperger, J. Phys. Chem. **34**, 669 (1930).

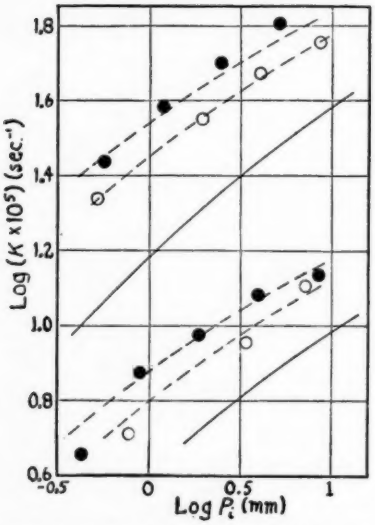

FIG. 1. Effect of deuterium. The solid curves are for pure azomethane at 310°C and 290.4°C. The broken curves are for deuterium mixtures, of the compositions given in Table I, assuming $\alpha=0.66$. At each temperature the black circles go up with the upper broken curve, the open circles go with the lower broken curve.

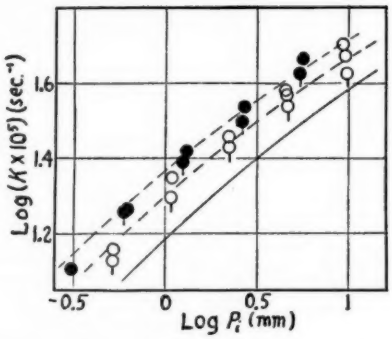

FIG. 2. Effect of nitrogen and of carbon monoxide. Solid line, pure azomethane, 310°C. Broken lines 5 : 1 and 10 : 1 mixtures with $\alpha=0.16$. Black circles, 10 : 1 mixtures. Open circles, 5 : 1 mixtures. Circles without tail, N_2. Circles with tail, CO.

especially with the composition of the mixture in the case of hydrogen (α increases with increasing percent of hydrogen). This is probably due, at least in part, to reaction of the methyl radicals, formed in the decomposition of the azomethane, with H_2, forming methane and releasing a hydrogen atom, which then reacts further, possibly with the azomethane. The amount of reaction is not so great but that an uncritical examination might lead one to believe that hydrogen is simply activating the azomethane; on the other hand it is sufficiently marked so that one would expect to observe variations of α also, if to a somewhat smaller extent, in the case of deuterium. We can only conclude from our results that either the methyl radical reacts much more slowly with deuterium, or else that the deuterium atom is less active than the hydrogen atom, and that this difference is great enough so that deuterium may be considered to be practically an inert gas. Tentatively, at least, we believe that the value of α obtained may be taken as giving the true indication of the relative activating efficiency of deuterium.

We have pointed out in our previous work that the constancy of α for helium over a range of conditions furnishes evidence that the azomethane decomposition is not a chain reaction, or at least that the chain length is independent of the pressure over the range of pressures studied. The results obtained in this paper reinforce this view. Particularly noteworthy in this connection are the data with carbon dioxide, in which the constancy of α is maintained not only over the usual pressure range but over a very considerable range in the composition of the mixtures used.

Let us now turn our attention to a consideration of the variation of α' for the different gases studied. Most striking is the difference between deuterium and helium and in particular the low efficiency of helium. On account of the almost complete spherical symmetry of the electron distribution in the outermost ranges of the deuterium molecule, it hardly seems possible that as great a difference as exists between these two gases can be due to the possibility of exchange of rotational energy by the deuterium. Though this can hardly be said to be proved, it suggests that a large part of the difference between helium and the other molecules in general is to be ascribed to the exchange of vibrational energy between molecules being a more probable process than a change from translational into vibrational energy, or *vice versa*.[8] The relatively

[8] It is of course still necessary, in general, for some transfer of energy between translational and vibrational types to take place, but the amount will be much less, and the theory (reference 11) indicates that it is easier for a small amount of energy to be so transferred than a large amount.

Added in proof: Since submitting this paper we have seen the article of Patat and Bartholomé, Zeits. f. physik.

small efficiency of helium finds a counterpart in the work of Koblitz and Schumacher[9] on the F_2O decomposition, but Volmer[4] and his co-workers[10] found that helium was a better activator than nitrogen or oxygen in the N_2O decomposition.

Some theoretical calculations on the exchange of translational and vibrational energy have been published by one of us.[11] The approximations it was necessary to make limit the range of applicability of these calculations, so that they probably cannot be counted upon to give information in cases in which the colliding body is heavier than helium. They brought out, however, the various factors upon which such probabilities depend—the mass of the colliding particle, the "sharpness" of the collision, the amount of energy transferred from translation to vibration, the nature of the vibrators, etc. These factors and others will enter in a still more complicated way when there is exchange of vibrational energy between oscillators, and the obvious difficulty in interpreting the results of various experimenters cited at the end of the preceding paragraph makes it seem futile to attempt a theoretical discussion of the values of α' at the present time. It may, however, be of interest to note that the compounds containing light atoms, which we may infer would tend to participate in "sharp" collisions, have the largest values of α' in our experiments, except for the very symmetrical methane. The low bending frequency of carbon dioxide does not seem to result in its having a large value of α', as might, off-hand, have been expected.

Perhaps the most remarkable feature about the results of the present paper, as well as those of Koblitz and Schumacher and Volmer and his coworkers, and also those of Schumacher and Sprenger[12] who studied the decomposition of NO_2Cl, is the small range of the values of α'. In particular we should like to call attention to the relatively small difference between nitrogen and carbon monoxide; as will be indicated by an inspection of Fig. 2 the difference between them is practically within the limits of experimental error. This is in marked contrast to results on the transfer of energy between carbon monoxide or nitrogen and chlorine,[13] and between carbon monoxide or nitrogen and oxygen[14] obtained from acoustical experiments. It must of course be noted that the processes occurring in acoustical experiments are rather different from those occurring in reaction rate experiments. The dispersion of sound depends upon the rapidity with which equilibrium is established between translational and vibrational degrees of freedom and hence measures the rate of transfer between vibrational and translational energy rather than between two types of vibrational energy. Furthermore simpler molecules have been studied acoustically and activated molecules are not involved. Nevertheless it is difficult to understand why reaction rate experiments and acoustical experiments give such different results. The writers of the acoustical papers have invoked two different hypotheses to explain their observations. The difference between the effects of carbon monoxide and nitrogen on oxygen has been ascribed to the electric moment of the former,[14] and the difference between their action on chlorine has been related to the fact that carbon monoxide and chlorine can be thought of as combining to form phosgene.[13] Whether these hypotheses can be considered reasonable on *a priori* grounds will depend upon whether the forces due to the dipole moment of carbon monoxide on the one hand, or the chemical forces between it and chlorine on the other, are comparable to the ordinary van der Waals and repulsive forces in the average collision at which energy is exchanged. In our opinion it is very unlikely that this is the case. If the dipole moment of carbon monoxide were of importance we should not expect the physical properties to be so similar to those of nitrogen. And it is well known that the chemical forces have in general a smaller range of action than the van der Waals and repulsive forces. When two chemically saturated molecules collide the first forces to

Chemie **B32**, 396 (1936), which is of interest in this connection.

[9] Koblitz and Schumacher, Zeits. f. physik. Chemie **B25**, 283 (1934).

[10] See Volmer and Bogdan, Zeits. f. physik. Chemie **B21**, 271 (1933).

[11] O. K. Rice, J. Am. Chem. Soc. **54**, 4558 (1932). See also Zener, Phys. Rev. **37**, 556 (1931).

[12] Schumacher and Sprenger, Zeits. f. physik. Chemie **B12**, 115 (1931).

[13] Eucken and Becker, Zeits. f. physik. Chemie **B27**, 261 (1934). See also Franck and Eucken, ibid. **B20**, 460 (1933).

[14] Kneser and Knudsen, Ann. d. Physik **21**, 682 (1934).

come into play are the van der Waals forces; at smaller distances the repulsive forces start to operate; at still smaller distance forces of the Heitler-London exchange type *may* become important, but the relative energy of the molecules must be large in order for them to get close enough for this to happen. It is true that the acoustical experiments indicate a slight positive temperature coefficient for the exchange of energy, so that it seems that molecules with excess relative energy exchange energy more readily, but the indicated activation energies are not very large and it seems unlikely to us that chemical forces can play a great role. If these considerations are correct, the transfer of energy may be thought of as taking place between two collections of atoms, the atoms in each group being tightly held together, and the interaction of the atoms of one group with those of the other being like an interaction between billiard balls—not hard billiard balls, to be sure, but "squashy" ones, this being essentially the assumption of Rice and Zener.[11] For an interaction of this sort carbon monoxide ought to resemble nitrogen, which accords fairly well with our results, but leaves the acoustical work unexplained.

Finally, we must make note of the great difference in the absolute values of the efficiency of energy transfer in the acoustical and the kinetic experiments. In the former the collision efficiency ranges from around 3×10^{-2} to about 10^{-6}, but most of the values are in the lower ranges. In the case of F_2O Koblitz and Schumacher have shown that the absolute collision efficiency is of the order of 1. Volmer has concluded in the case of N_2O that perhaps only one collision in 200 of an activated molecule leads to deactivation. However, if not all the degrees of freedom of N_2O, but rather only one, is involved in the reaction, then the calculated number of activated molecules becomes smaller and it would be possible to assume an efficiency[15] of 1 for deactivation of N_2O by N_2O. Since N_2O is a linear molecule it seems quite likely that there is no transfer of energy between stretching and bending vibrations. Furthermore, the decomposition of N_2O presumably does not involve the breaking of a bond, but rather a predissociation. This predissociation is probably very definitely associated with one particular normal (or approximately normal) vibration, in contrast to the breaking of a bond. It has previously been suggested that only one vibration is concerned (at least at high pressures) in the case of the decomposition of NO_2Cl, which also probably involves a predissociation.[16] In the case of the azomethane decomposition, on account of the great number of degrees of freedom involved, the range of their frequencies, and the fact that the bimolecular stage of the reaction is never reached experimentally, it is not practical to attempt to make a very accurate estimate of the number of activated molecules, and hence it is not possible to say just what the deactivational efficiency is, but there is no evidence against its being of the order of 1, and this would make the efficiency of helium fairly close to what might be expected from the calculations of Rice.

§4. Preliminary Notice of Experiments with Reacting Gases

We should like to note here some results obtained with gases which apparently are not inert. We have already observed that in the case of hydrogen α does not appear to be constant. A similar result was found with ethane as the "inert" gas, but in this case α seemed to depend most strongly on the pressure in a given mixture, increasing as the pressure decreased. Our values were not only not constant, but in all cases were lower than those found by Ramsperger.[7] It is possible that Ramsperger's ethane contained some diethyl ether, as he used this as a solvent in preparing his ethane, while we used the higher boiling dibutyl ether. We obtained results with propane which were very similar in every detail to those obtained with ethane. But, in marked contrast, azomethane starts a chain decomposition in isobutane.

The inconstancy of α in the cases of ethane and propane is presumably due to the occurrence of side reactions. These side reactions probably

[15] Ramsperger and Waddington, Proc. Nat. Acad. Sci. **17**, 103 (1931); Hunter, Proc. Roy. Soc. **A144**, 386 (1934), however, does not agree with Volmer and his collaborators on the activation energy for this reaction. In view of this fact and the correction which a change of the activation energy would entail, the case of N_2O may be in some doubt.

[16] O. K. Rice and Sickman, J. Am. Chem. Soc. **56**, 1450 (1934).

result from the presence of methyl radicals which can remove a hydrogen atom from many organic molecules, forming methane and a more complicated free radical which may then react further. The great difference in the effect of methyl radicals on various organic substances, some of them quite similar, is of considerable interest. Azomethane itself is presumably very little attacked if at all. It is impossible to say whether methane reacts with methyls or not as the products would be the same as the reactants. Ethane and propane are presumably only slightly attacked by methyls, but isobutane, acetaldehyde[17] and propionaldehyde[18] are so readily attacked at the temperature at which azomethane decomposes that the side reaction becomes a main reaction. It is, of course, to be remarked that relatively small differences in the activation energies involved would account for the observed effects.

[17] Allen and Sickman, J. Am. Chem. Soc. **56**, 2031 (1934).
[18] O. K. Rice and Sickman, J. Am. Chem. Soc. **57**, 1384 (1935).

The kinetics of the polymerization of ethylene induced by methyl radicals from azomethane has already been described in outline.[18] It should be remarked that it is the over-all rate of change of pressure with time which is proportional to the square root of the azomethane pressure and the three-halves power of the ethylene pressure. When an attempt is made to correct for the increase of pressure produced by the decomposition of azomethane this simple relation seems to be upset.

Azomethane also causes propylene to polymerize. The reaction is, we believe, similar to the ethylene polymerization. Acetylene also polymerizes under the influence of methyl radicals from azomethane, the rate of pressure change being proportional to the square root of the azomethane pressure and to the first power of the acetylene pressure, a rather more usual result. These various reactions will be described in detail later.

Erratum. In Part II an error was made in the calculations for Run 217. For this run $\log P_i$ should be 0.295 and $\log (K \times 10^5)$ should be 0.691.

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The Effect of Structure Upon the Reactions of Organic Compounds. Temperature and Solvent Influences

LOUIS P. HAMMETT, *Department of Chemistry, Columbia University*

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The effect of a substituent upon the heat of ionization of an organic acid is far from identical with its effect upon the free energy of ionization. In the case of benzoic acid derivatives the entropy of ionization varies with structure in a way which can be predicted from the temperature dependence of the dielectric constant of the solvent, and which is closely correlated with the effect of a change in the dielectric constant of the solvent upon the relative strengths of substituted and unsubstituted acids. The behavior of aliphatic acids is more complicated, probably because of their less rigid structure. Similar considerations apply to the effect of changes in structure of reactant upon other equilibria and upon reaction rates.

THE effect of a change in structure of reactant upon the equilibrium or rate of an organic chemical reaction has been interpreted in a variety of ways.[1] Thus the shift in the ionization constant of formic acid produced by the substitution of another group for the nonionizable hydrogen has been attributed to an increase or decrease in the electrical work involved in separating the ions of the acid which results either from the dipole field of the substituent or from internal electron displacements of various sorts produced by the substitution. These interpretations have in common an identification

[1] See for instance: Waters, *Physical Aspects of Organic Chemistry* (New York, 1936); or Ingold, Chem. Rev. **15**, 225 (1934).

TABLE I. *Reference acid formic acid.*

Acid RCOOH	K	ΔF	ΔH	ΔS	$-.005\Delta F$	ΔpK
Acetic	0.0990	+1372	−99	−4.94	−6.9	+0.13
Propionic	0.0754	+1533	−155	−5.67	−7.7	+0.40
Butyric	0.0855	+1460	−678	−7.17	−7.3	+0.37
Chloracetic	7.78	−1216	−1157	+0.20	+6.1	+0.27
Glycollic	0.833	+109	+223	+0.38	−0.55	——
Lactic	0.775	+147	−14	−0.64	−0.74	——

TABLE II. *Reference acid benzoic acid.*

Acid XC_6H_4COOH	K	ΔF	ΔH	ΔS	$-.005\Delta F$	ΔpK
m-NO_2 benzoic	5.24	−980	+350	+4.5	+4.9	−0.35
m-I benzoic	2.00	−410	+90	+1.7	+2.1	−0.22*
m-CH_3 benzoic	0.85	+100	+120	0.0	−0.5	+0.04
p-OCH_3 benzoic	0.50	+410	+110	−1.0	−2.1	+0.12
p-CH_3 benzoic	0.68	+230	+210	0.0	−1.2	+0.04
o-NO_2 benzoic	96.4	−2690	−2960	−0.9	+13.5	+0.27
o-OH benzoic	15.6	−1630	+670	+7.7	+8.2	−0.27
o-I benzoic	19.8	−1770	−2310	−1.8	+8.9	——
o-Cl benzoic	19.3	−1750	−2290	−1.8	+8.8	+0.28
o-CH_3 benzoic	1.93	−390	−1230	−2.8	+2.0	+0.28

* This is the value for m Cl-benzoic. The value for m-I benzoic should be nearly identical.

of the effect of the substituent upon the electrical work with its effect upon the free energy of the reaction, an identification whose theoretical correctness is not beyond question. It would be justified (except for the effect of possible differences in zero-point energy) were the effect of the substituent upon the free energy equal to its effect upon the heat of the reaction, as has been not infrequently supposed to be the case. Actually however, as the data in Tables I and II demonstrate, no such equality exists.

Table I contains under the heading K the equilibrium constants at 25°C for the series of reactions

$$RCOOH+HCOO^-\rightleftarrows RCOO^-+HCOOH. \quad (1)$$

The quantity K is of course the ratio of the ionization constant of the acid named to that of the reference acid formic acid. Under the headings ΔF, ΔH, and ΔS are given the changes in free energy, in heat content, and in entropy for the same series of reactions, all at 25°C. These quantities measure the effect of the substitution of the group R for hydrogen upon the free energy, heat content, and entropy of ionization. The data in this table derive from the recent very accurate work of Harned and co-workers and of Nims and co-workers,[2] and their carefully fitted empirical equations for the temperature variation of the ionization constant were used in calculating the heats of ionization and entropies given in the table.

Table II contains similar information for the series of reactions

$$XC_6H_4COOH+C_6H_5COO^- \rightleftarrows XC_6H_4COO^-+C_6H_5COOH \quad (2)$$

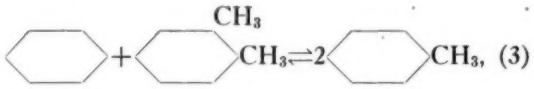
and the quantities given represent therefore the effect of a substituent in the benzene ring on the ionization of benzoic acid. The table is based upon the work of Schaller,[3] which, while it is certainly less precise than Harned's work, does represent measurements by a single careful investigator under constant conditions and in the same apparatus at approximately 10° intervals from room temperature to the boiling point. Under these conditions many of the errors which might affect the results as absolute measures of ionization constant or of its temperature coefficient vanish when, as in the present case, only the ratios of ionization constants are considered. Over the range and within the precision of these measurements the plot of log K against $1/T$ is linear, and the values of ΔH in the table were obtained graphically from such plots. The same relationship is nearly but not quite valid within the precision of Harned's work. It follows that the difference in the heats of ionization of two carboxylic acids is nearly independent of temperature, although the heat of ionization of a single acid varies rapidly with temperature.

These results are at first sight extremely discouraging for any attempt at theoretical interpretation. The entropy changes are large, equivalent to one or even two orders of magnitude in the ionization constant, and the heats of ionization show no relation whatsoever to the free energies. An "electronic theory" of the effect of substituents based upon the heats of reaction would be in striking contradiction to one based upon ionization constants, most notably in the case of m-nitro benzoic acid. Such large entropy changes might arise from the internal motions of the acids and the corresponding anions, for the

[2] Harned and Embree, J. Am. Chem. Soc. **56**, 1042 (1934); Harned and Ehlers, ibid. **54**, 1350 (1932); **55**, 652, 2379 (1933); Harned and Sutherland, ibid. **56**, 2039 (1934); Wright, ibid. **56**, 314 (1934); Nims, ibid. **58**, 987 (1936); Nims and Smith, J. Biol. Chem. **113**, 145 (1936).

[3] Schaller, Zeits. f. physik. Chemie **25**, 497 (1898).

recent data of Kassel[4] shows that the reaction



which has the same sort of symmetry as the reactions of Eqs. (1) and (2), is accompanied by an entropy change of 5.9 units in the gas state. There are however indications that, in the case of the rigid structures of the benzoic acid derivatives, the entropy change depends chiefly upon the solvent and can be accounted for in terms of the temperature dependence of its dielectric constant.

The hypothesis that the change in ionization constant produced by a substituent results from the effect of its dipole field upon the potential energy of the hydrogen ion has been suggested several times.[5] the equation which gives it expression is

$$\Delta F = e\Delta(\mu \cos\theta)/Dr^2, \qquad (4)$$

where ΔF has the same significance as in Tables I and II, $\Delta(\mu \cos\theta)$ is the difference between the components in the direction of the carboxyl group of the dipole moments of the X−C and H−C groups, r is the distance from the dipole to the carboxyl group, and D is the dielectric constant. It is not however a satisfactory equation. In the first place the quantity $\Delta(\mu \cos\theta)$ should be just equal to the total moment of the substance C_6H_5X in the case of a *para* substituted benzoic acid derivative in which the moment of the substituent is directed toward or away from the center of the benzene ring. But substitution of the moments of various benzene derivatives into Eq. (3) along with a value of 80 for D and a reasonable figure (6A) for r leads to values of ΔF for the corresponding *para* derivative of benzoic acid about ten times too large. Furthermore as Dippy and Watson[6] have shown the relation between dipole moment of C_6H_5X and free energy of ionization of XC_6H_4COOH is not a linear one, nor indeed even a unique correlation. This result is not surprising for a number of reasons, of which the most fundamental is the fact that the identification of an electrical potential energy which involves a temperature dependent dielectric constant with a free energy change can at best give an approximate result. That it may be a useful approximation and even an accurate one for large distances appears from the success of the Debye-Hückel theory of electrolytes, in which the same identification is made.

Schwarzenbach[7] has attempted to account for dielectric saturation and for the transmission of the field through the solute molecule by a modified equation in which the actual dielectric constant possessed by the solvent in bulk is corrected and the corrected value is used in Eq. (4). He has verified some of the corollaries of the modified equation in a most ingenious fashion by comparing the effects of substitution upon the ionization of phenols and of thiophenols.

It is possible however to account for the entropies of ionization as well as for the effects observed by Schwarzenbach by a different modification

$$\Delta F = A/Dr^2. \qquad (5)$$

The quantity A is characteristic of a given substituent and position, is independent of temperature, and its magnitude is very approximately proportional to, but several times larger than, the value of $\Delta(\mu \cos\theta)$. The equation is of course a first-order empirical correction of the inadequate Eq. (4), which is to be justified by its results. It differs from Schwarzenbach's equation by putting the burden of the correction on the $\Delta(\mu \cos\theta)$ factor rather than on D.

Differentiating Eq. (5) with respect to temperature

$$\frac{\delta \Delta F}{\delta T} = -\frac{A}{D^2 r^2}\frac{\delta D}{\delta T} = -\Delta F \frac{\delta \ln D}{\delta T}$$

and

$$\Delta S = \Delta F \frac{\delta \ln D}{\delta T}. \qquad (6)$$

Since the quantity $\delta \ln D/\delta T$ has the value -0.005 for water this treatment predicts an entropy change equal to the free energy change times -0.005. The sixth column of Tables I and II shows a fairly satisfactory verification for the *meta* and *para* derivatives of benzoic acid, but a

[4] Kassel, J. Chem. Phys. **4**, 276 (1936).
[5] For a review of the literature see Wooten and Hammett, J. Am. Chem. Soc. **57**, 2289 (1935).
[6] Dippy and Watson, J. Chem. Soc. 436 (1936).
[7] Schwarzenbach and Egli, Helv. Chim. Acta **17**, 1184 (1934); Schwarzenbach and Epprecht, ibid. **19**, 493 (1936).

complete failure for the *ortho* derivatives of benzoic acid and for the aliphatic acids.

If now we suppose that a substituent may have a further effect upon the work of ionization which is independent of medium and temperature we obtain

$$\Delta F = A/Dr^2 + C, \tag{7}$$

from which we get

$$\Delta S = \frac{A}{r^2}\left(\frac{1}{D^2}\frac{\delta D}{\delta T}\right) \tag{8}$$

for the temperature effect and

$$\Delta F_1 - \Delta F_2 = \frac{A}{r^2}\left(\frac{1}{D_1} - \frac{1}{D_2}\right) \tag{9}$$

for the effect of a transfer from a medium of dielectric constant D_2 to one of constant D_1. Consequently

$$\frac{\Delta S}{\Delta F_1 - \Delta F_2} = \frac{D_2}{(D_2 - D_1)D_1}\frac{\delta D_1}{\delta T}, \tag{10}$$

and the ratio of the entropy change in one solvent to the difference in the free energy changes in two solvents of different dielectric constants should be independent of the substituent X.

The only extensive data for a test of this relation are contained in the work of Wooten and Hammett[8] on the relative ionization constants of various acids in the solvent butyl alcohol in the presence of a considerable concentration of neutral salt. The effect of the salt is to alter all ionization constants in much the same way that an increase in dielectric constant would. This follows from the fact that the clustering of alkali ions around the acid anions is determined by the same field which determines the potential energy of the hydrogen ion, and that the effect of the field upon the alkali ions must produce a change in free energy of ionization which is opposite in sign to that produced by the effect upon the hydrogen ions.

In general therefore it is to be expected that the linear relation between ΔF and $1/D$ discovered by Wynne-Jones,[9] which is entirely in agreement with Eq. (7), will be more valid the lower the ion association. That is to say, it should be most satisfactory in solvents of relatively high dielectric constant and the ionization constant should in any case be the limiting value for zero ionic strength.

Because of the effect of the salt we cannot test Eq. (10) with respect to the numerical value of the right-hand side, since we cannot expect to use the actual value of the dielectric constant of butyl alcohol. We may nevertheless predict that the ratio of ΔS to the ΔpK of Wooten and Hammett, which equals $-(\Delta F_1 - \Delta F_2)/2.3RT$ will be independent of the substituent, negative in sign, and greater in magnitude than the value 1.9 calculated for $D_1 = 80$ and $D_2 = 17.4$.

As a comparison of columns 5 and 7 of Tables I and II show this prediction is fairly well verified (probably within the precision of Schaller's work) for *ortho* as well as for *meta* and *para* substituted benzoic acid derivatives, with the exception of salicylic acid, but is entirely invalid for the aliphatic acids. The obvious interpretation of this result is that the simple assumptions used which include a neglect of the internal motions of the reactant molecules are valid only for the rigid structures of the benzoic acid derivatives. The considerable deviation in the case of salicylic acid may well depend upon some specific interaction between the adjacent hydroxyl and carboxyl groups, perhaps of the nature of a hydrogen bond.[10]

The validity of Eq. (5) for the *meta* and *para* derivatives shows that the quantity C in Eq. (7) must be zero or nearly so for these substitutions, whereas it is certainly not zero for *ortho* substitutions. This contrast between the effects of close and distant substitutions is an extension to benzoic acid derivatives of a conclusion which Schwarzenbach and Egli[7] have previously reached from a study of phenols and thiophenols. There also it was found that *ortho* substituents exert large and specific effects which cannot possibly be attributed to dipole fields.

When we consider other reactions than the ionization of acids we find that Eq. (5) is insufficient even for *meta* and *para* substituents. This follows both from the fact that substituents

[8] Wooten and Hammett, J. Am. Chem. Soc. **57**, 2289 (1935).

[9] Wynne-Jones, Proc. Roy. Soc. **A140**, 440 (1933).

[10] See Branch and Yabroff, J. Am. Chem. Soc. **56**, 2568 (1934).

do have an effect upon reactions in which neither reactants nor products are electrically charged and also from the fact that the effect of a substituent upon one reaction may be many times greater than it is upon another. For instance the free energy of the process

$$XC_6H_4NH_3^+ + C_6H_5NH_2 \rightleftarrows XC_6H_4NH_2 + C_6H_5NH_3^+ \quad (11)$$

is three times as great for the same substituent X, provided this occupies the *para* or *meta* position, as it is for the reaction of Eq. (2).[11]

Since the distance between substituent and dissociable hydrogen does not differ enough in the two cases to account for this effect, the linear relation between the free energies of the two series of reactions requires an equation of the following form for the free energy:

$$\Delta F = \frac{A}{r^2}\left(\frac{1}{D} + B\right). \quad (12)$$

The quantity B is of the nature of a function of the polarizabilities of the linkages being made and broken in the reaction. It is independent of temperature and medium, and its magnitude must be of the order of twice that of the term $1/D$ in the case of the reaction of Eq. (11). It follows that while entropy and medium effect should have the same absolute value for reaction (11) as for reaction (2), they will represent considerably smaller fractions of the free energy in the former case.

Data are not available for a test of this prediction for the ionization of aniline derivatives, but it can be tested by studies of reaction rates and their temperature variation. It is now apparent from the work of Scheffer and Brandsma,[12] of La Mer,[13] and of Eyring[14] that a reaction rate problem is essentially similar to an equilibrium one. In the rate problem the quantity $-RT \ln k_1/k_2$, where k_1 and k_2 are rate constants for the reaction of substituted and of unsubstituted reactant is equivalent to our ΔF; the difference in the Arrhenius activation energies for the two reactions is equivalent to our ΔH; and the difference in the entropies of activation to our ΔS. In the recently studied case of the alkaline hydrolysis of benzoic esters,[15] the quantity $-RT \ln k_1/k_2$ must include the electrical work involved in transferring a hydroxyl ion from the activated complex of hydroxyl ion with substituted ester to the complex of hydroxyl ion and unsubstituted ester. This electrical work must be very nearly the same as the electrical work involved in reaction (2), which as we have seen is practically identical with the free energy change of that reaction. Since, however, the quantity $-RT \ln k_1/k_2$ for the ester reaction is 2.5 times the ΔF for the ionization reaction (2),[16] the quantity B of Eq. (12) must equal 1.5 times $1/D$ for the hydrolysis reaction. It is therefore easy to see why, as Ingold and Nathan[15] have observed, the changes in entropy of activation are small for this series of reactions compared with the changes in free energy of activation, or that, what amounts to the same thing, the changes in the factor P of the English workers will be small compared with the changes in k. By contrast the reactions of alkyl halides studied by Winkler and Hinshelwood[17] present a situation much like that of the ionization of the aliphatic acids. Changes in the entropy of activation or in the P factor are relatively large, are unpredictable, and probably depend upon the internal motions of the reactants and of the activated complex as well as upon the solvent molecules.

[11] This is one of a large number of simple linear relations between the effects of substituents upon various reactions of benzene derivatives. Attention to some of these has previously been called by myself, Chem. Rev. **17**, 125 (1935), and by Burkhardt, Ford, and Singleton, J. Chem. Soc. 17 (1936). This subject will be discussed in detail in another paper.

[12] Scheffer and Brandsma, Rec. trav. chim. **45**, 522 (1926); Brandsma, ibid. **47**, 94 (1928); **48**, 1205 (1929).
[13] La Mer, J. Chem. Phys. **1**, 289 (1933).
[14] Eyring, J. Chem. Phys. **3**, 107 (1935).
[15] Ingold and Nathan, J. Chem. Soc. 222 (1936).
[16] Hammett, Chem. Rev. **17**, 125 (1935).
[17] Winkler and Hinshelwood, J. Chem. Soc. 1147 (1935).

The Crystal Structure of Germanium Disulphide

W. H. ZACHARIASEN, *Ryerson Physical Laboratory, University of Chicago*

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Crystals of GeS_2 are orthorhombic. The unit cell contains 24 molecules and has dimensions: $a=11.66$A, $b=22.34$A, $c=6.86$A. Accuracy $\frac{1}{2}$ percent. The space groups is Fdd (C_{2v}^{19}). Eight of the germanium atoms are situated on the twofold axes; all other atoms occupy general positions. The twelve parameters involved have been determined. Every germanium atom is tetrahedrally linked to four sulphur atoms, with an interatomic distance of 2.19A. The angle between the two sulphur bonds is 103°. A three-dimensional network somewhat similar to the silica networks is formed.

THE material of germanic sulphide used in this investigation was presented to us by Professor W. C. Johnson of the Chemistry Department of this University. The sample consisted of crystal aggregates with occasional needle-shaped single crystal skeletons. Using the latter we succeeded in obtaining a set of oscillation photographs around one of the crystallographic axes, (b).

The crystals proved to be orthorhombic with the following dimensions of the pseudo hexagonal unit cell:

$$a=11.66\pm0.05\text{A}, \quad b=22.34\pm0.10\text{A}, \quad c=6.86\pm0.03\text{A}.$$

The density was determined by the suspension method (using as suspension liquid methylene iodide diluted with toluene) to be 3.01. This gives 24 molecules per unit cell.

The translation lattice proved to be face centered. Furthermore reflections HOL and OKL were found to be absent unless $H+L$ resp. $K+L$ be divisible by four. The latter observations require the two vertical axial planes (the X and Y planes) to be glide planes with translations $\frac{1}{4}(b+c)$ and $\frac{1}{4}(a+c)$. Since the unit cell contains so many atoms it is reasonable to suppose that some of them occupy general space group positions. Hence the space group is $Fdd(C_{2v}^{19})$.[1]

Eight of the 24 germanium atoms per unit cell must lie on the twofold axes: $(000)_f$ $(\frac{1}{4}\frac{1}{4}\frac{1}{4})_f$. Further atoms may not be placed in special positions as interatomic distances along the z axis will become too short. Thus one set of 16 germanium atoms and three sets of 16 sulphur atoms have to be placed in general positions:

$$(xyz)_f \quad (\bar{x}\bar{y}z)_f \quad (\tfrac{1}{4}-x, \tfrac{1}{4}+y, \tfrac{1}{4}+z)_f \quad (\tfrac{1}{4}+x, \tfrac{1}{4}-y, \tfrac{1}{4}+z)_f$$

and we have twelve unknown parameters to determine.

To a first approximation we may attribute the intensity of reflection to the germanium atoms

TABLE I. *Parameter values.*

	$2\pi x$	$2\pi y$	$2\pi z$
Ge_{II}	45°	50°	0°
S_I	8	29	66
S_{II}	55	−5	−66
S_{III}	22½	45	−100

TABLE II. *Observed intensities and calculated amplitudes.**

H L \ K	either 1 or 0	3 2	5 4	7 6	9 8
0 2	0 nil	9 vvw	0 nil	47 s	0 nil
1 1	44 vs	13 w.	22 m	37 s	
2 0	0 nil		16 w	0 nil	10 vw-
3 1	34 m	26 m	12 vw-	6 vvw	24 w.
2 2	22 w.	29 w.	41 m-	17 w.	16 w
4 0	19 w.	26 m-	39 s	11 nil	26 m
1 3	24 w	21 w	20 w-	33 m.	34 m
4 2	0 nil	32 w.	8 vw-	15 vw-	9 vw-
5 1	23 w	32 w.	36 m	6 vw-	
3 3	18 w-	31 w.	31 m-	18 vw-	34 w
6 0	0 nil	36 w.	25 w	18 w.	23 w
0 4	57 m	0 nil	39 m-	0 nil	49 m-
6 2	12 w.	49 m.	9 nil	33 wm	26 w-
2 4	0 nil	20 w	13 nil	19 w-	21 w
5 3	21 vw-	33 w	29 w	4 vw	
7 1	29 wm	10 nil	3 nil	29 m-	

* In calculating the amplitudes values for the scattering powers of germanium and sulphur were taken from the compilation by R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1932).

[1] W. C. Johnson, Zeits. f. anorg. Chemie **216**, 273 (1934), reports the results of our determination of the cell size, density and space group. We have since interchanged the second and third axes so as to agree with the common practice of choosing the Z axis along the twofold axis of point group C_{2v}.

alone. This assumption is based upon the facts that the scattering power of germanium is roughly twice that of sulphur, and that the chance of getting appreciable cooperation from the sulphur atoms is small owing to the many degrees of freedom involved (nine degrees of freedom for sulphur, only three for germanium). Naturally the assumption is only statistically valid, so that conclusions based upon it must be drawn from a great number of observations. In this manner we easily found the parameter values for germanium. By a series of successive approximations we succeeded in obtaining fairly accurate values for the nine sulphur parameters. The parameter values are given in Table I. Table II shows a comparison between observed intensities and calculated amplitudes. Trial shows that the atomic coordinates have been determined to an accuracy of about 0.05A.

In Fig. 1 is shown a projection of the structure on the XY-plane.

Every germanium atom is bonded to four sulphur atoms situated at the corners of slightly distorted tetrahedra with germanium at the center. The interatomic distance Ge-S is 2.19A. The sum of the "covalent" radii given by Pauling and Huggins is 2.25A.[2] The Ge-S distance in the monosulphide is considerably greater, namely 2.47A and 2.64A.[3] Every sulphur atom is linked to two germanium atoms, the bond angle being 103° (98°, 104° and 107°). This value is entirely inexplicable unless we assume the binding to be predominatingly covalent. The Ge-Ge interaction prevents the bond angle from assuming the ideal value of 90°.

The GeS_4 tetrahedra are linked together (by sharing corners only) so as to form a three-dimensional tetrahedral network, somewhat similar to the networks found for SiO_2 in its various forms. It differs from these in the value of the bond angle, which in low quartz is 144°, in the other forms still larger.[4] This difference is simply an expression for the difference in the nature of the bonds Si-O and Ge-S. In the former the ionic contribution to the binding will be considerably more important than in the latter case. (The high polarizability of the sulphur ion with a corresponding transfer of charge from sulphur to germanium is incompatible with a high ionic contribution to the bond.)

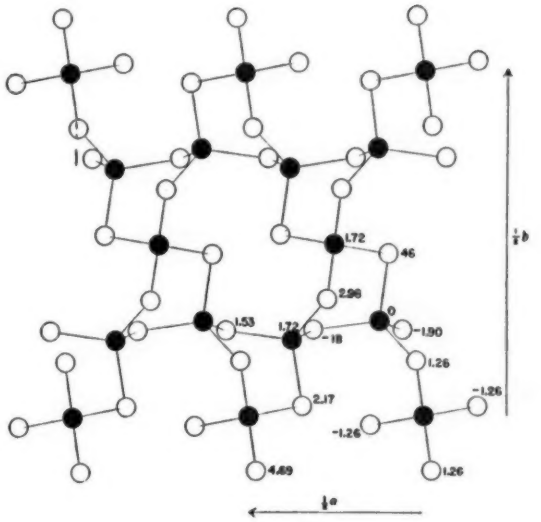

FIG. 1. shows a projection on the c-plane of the atoms in half a unit cell. Germanium and sulphur atoms are represented by filled and open circles, respectively. For some of the atoms the height in A above the plane $z=0$ is given.

The GeS_2 structure is entirely different from the one recently reported for SiS_2, where the SiS_4 tetrahedra form endless chains by sharing edges with each other. The bond angle for sulphur in SiS_2 has the surprisingly low value of 80°.[5]

The greater part of the work connected with this investigation was carried out during the tenure of a fellowship of the Guggenheim Foundation.

[2] L. Pauling and M. L. Huggins, Zeits. f. Krist. **87**, 205 (1934).
[3] W. H. Zachariasen, Phys. Rev. **40**, 917 (1932).
[4] Péi-Hsiu Wei, Zeits. f. Krist. **92**, 355 (1935).
[5] W. Büssem, H. Fischer, E. Gruner, Naturwiss. **43**, 740 (1935).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

Note on Absorption Processes in the Halogen Spectra

The interesting work of Acton, Aickin and Bayliss on the continuous absorption of bromine, which the writer has had the privilege of reading in manuscript, makes it easier than before to understand the electronic transitions involved in the halogen spectra. A.A.B. find the visible absorption continuum of Br_2 for $v''=0$ to be composite, with a stronger component A having its maximum near λ4150, and a second component B of about a third or a fourth as large an integrated intensity as A, and with maximum near λ4950 (cf. their Fig. 2). They offer two possible explanations, of which they favor the second: (1), B and A, respectively, represent $^3\Pi_1 \leftarrow {}^1\Sigma^+$ and $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$; (2), B and A represent $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ and $^1\Pi \leftarrow {}^1\Sigma^+$, respectively. A.A.B. also suggest that interpretation (2) may be extended to I_2 and Cl_2.

In the present note it will be shown that while explanation (2), somewhat modified, may (or may not) be applicable to Br_2 and Cl_2, it is inapplicable to I_2; but that in any case the results of A.A.B., taken in connection with theoretical considerations, show that the transition $^1\Pi \leftarrow {}^1\Sigma^+$ in the halogens is not so anomalously and universally weak as earlier data had indicated.

Let us first consider A.A.B.'s explanation (1) for Br_2. If this is correct, then the transition $^3\Pi_1 \leftarrow {}^1\Sigma^+$ (region B) is fairly strong. If this is true, the corresponding transition $^1\Pi \leftarrow {}^1\Sigma^+$ must, according to theory, be as strong or stronger. For $\Omega-s$ or case c or an intermediate type of coupling (let us call these cases α), $^3\Pi_1 \leftarrow {}^1\Sigma^+$ and $^1\Pi \leftarrow {}^1\Sigma^+$ would be about equal in intensity, while for ideal $\Lambda-\Sigma$ coupling (call this β), $^3\Pi_1 \leftarrow {}^1\Sigma^+$ should be vanishingly weak compared with $^1\Pi \leftarrow {}^1\Sigma^+$.[2] It is reasonable in Br_2 to expect a case roughly half-way between β and α, perhaps most likely nearer α.[2] It is then clear that A.A.B.'s explanation (1) must be modified by attributing a considerable part, probably about half, of the strong component A of the continuum to $^1\Pi \leftarrow {}^1\Sigma^+$, the remainder being $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$. This requirement that component A must itself be composite is not necessarily in contradiction to the apparent singleness of A, since with Ω–s coupling one expects the potential energy curves of $^3\Pi_{0^+}$ and $^1\Pi$ to run close together.

As a matter of fact, however, although A.A.B.'s absorption coefficient curve for $v''=0$ (their Fig. 2) does not show compositeness in A, their curve for $v''=1$ (their Fig. 3) does give decided evidence that three upper electronic states are involved in A and B. Although only three maxima are shown in their Fig. 3 curve, their *data* indicate that the highest frequency maximum of these is really double (see experimental points in Fig. 3); they consider, to be sure, that this doubling is not incapable of being explained by experimental error. If this double maximum is real, its higher frequency component may be attributed to $^1\Pi \leftarrow {}^1\Sigma^+$, the lower frequency component to $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$. The two remaining maxima in Fig. 3 are then readily explained, the middle one involving contributions from all three electronic transitions. On the whole we see that A.A.B.'s explanation (1), modified by the admission of $^1\Pi \rightarrow {}^1\Sigma^+$ as a strong transition, has strong support.

As A.A.B. point out, explanation (1) meets a serious difficulty in connection with the application of the Franck-Condon principle.[1] This can be slightly ameliorated, but not overcome, when the modification just given is introduced, according to which A is double. This difficulty is overcome, however, if explanation (2) is adopted. The strong maximum A must then be attributed to $^1\Pi \leftarrow {}^1\Sigma^+$ alone. The apparent doubling of the high frequency maximum in Fig. 3 has to be attributed now to experimental error. In their explanation (2), A.A.B. attribute B to $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ and consider that $^3\Pi_1 \leftarrow {}^1\Sigma^+$ is weak and lies at longer wave-lengths. It should, however, be noted that if $^3\Pi_1 \leftarrow {}^1\Sigma^+$ is weak compared with $^1\Pi \leftarrow {}^1\Sigma^+$, then we have nearly β type (Λ–Σ) coupling; but for Λ–Σ coupling, levels $^3\Pi_1$ and $^3\Pi_{0^+}$ in Br_2 should be rather close together (about 0.14 ev apart).[2] Thus if explanation (2) is essentially correct, we must probably suppose that the weak component B is really an unresolved composite of $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ and $^3\Pi_1 \leftarrow {}^1\Sigma^+$. While all this is not untenable, it appears somewhat unlikely that the coupling departs so far from α, and approaches β so nearly, as seems to be required by explanation (2). On the whole, explanation (2) seems less probable than (1), but the Franck-Condon argument in favor of (2) is strong. A more accurate knowledge of the potential energy curve of the $^3\Pi_{0^+}$ state, based on an analysis of data from the discrete Br_2 bands by the Rydberg-Klein method, should help to resolve this difficulty.

In the case of I_2, the intense part of the absorption curve (partly continuum, partly bands) shows a shoulder on its long wave-length side, similar to that in the Br_2 continuum, and suggests that, again, the absorption involves two upper electronic states. Recent work of Rabinowitch and Wood, however, shows that this shoulder is only slight when the

absorption coefficient is correctly determined in the region of the discrete bands.[3] It appears probable that this slight shoulder can be explained by the effects of excited lower vibrational states ($v''>0$), but this explanation ought to be tested by an analysis of absorption curves at several temperatures.

This I_2 absorption in the visible region is in all probability $^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$ almost entirely, overlain by a faint $^1\Pi\leftarrow{}^1\Sigma^+$ component.[2] That the latter must be faint is shown by the low intensity of the $^3\Pi_1\leftarrow{}^1\Sigma^+$ bands and continuum, taken together with the fact that the coupling in I_2 can hardly be very far away from α, i.e., intermediate between $\Omega-s$ and case c. With such coupling, $^1\Pi\leftarrow{}^1\Sigma^+$ should be of about the same intensity as $^3\Pi_1\leftarrow{}^1\Sigma^+$. [The $^3\Pi_1\leftarrow{}^1\Sigma^+$ continuum shows signs of a weak maximum, according to Brown, at λ7320.]

As an alternative explanation analogous to (2) for Br_2, A.A.B. suggest that one might attribute the weak λ7320 peak to $^3\Pi_1\leftarrow{}^1\Sigma^+$, the shoulder on the main I_2 absorption to $^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$, and the main peak to $^1\Pi\leftarrow{}^1\Sigma^+$. This, however, can hardly be accepted, since it would make $^1\Pi\leftarrow{}^1\Sigma^+$ enormously stronger than $^3\Pi_1\leftarrow{}^1\Sigma^+$, which would be possible only for Λ–Σ coupling. Aside from the general unreasonableness of such coupling for the $^{3,\,1}\Pi$ of I_2, it is to be noted that the empirical interval $^1\Pi-{}^3\Pi_{0^+}$ given by this interpretation is too small, and the empirical interval $^3\Pi_{0^+}-{}^3\Pi_1$ too large, to accord with Λ–Σ coupling.[2] Moreover, the Franck-Condon principle argument in the case of I_2 (unlike that of Br_2), favors the attribution of the main peak to $^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$, especially in view of the fact that the recent work of Rabinowitch and Wood locates this peak at λ5200 rather than at its previously accepted value λ5060. Hence there can be no reasonable doubt that the A.A.B. interpretation (2) must be rejected for I_2.

For Cl_2 either interpretation (1) or (2) appears to be consistent with existing data. According to (1), the continuum is mainly $^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$, while according to (2) it is mainly $^1\Pi\leftarrow{}^1\Sigma^+$. In any case, it seems clear that $^1\Pi\leftarrow{}^1\Sigma^+$ in Cl_2 is weaker than in Br_2. In F_2 it is still weaker.

All in all, the work of A.A.B. appears to establish that $^1\Pi\leftarrow{}^1\Sigma^+$ is fairly strong in Br_2, and stronger there than for any of the other halogens X_2. This relieves us of the previously existing onus of finding a systematic explanation for the apparent surprising weakness of this transition in all X_2. In the light of the work of A.A.B., it can be stated that the intensity of the transition $^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$ is a maximum for I_2, is much weaker in Br_2, and is probably still weaker, *perhaps* very much weaker, in Cl_2 and F_2. This is explainable by diminution in case c tendency from I_2 toward F_2, the occurrence of $^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$ at all being attributable (Van Vleck) to perturbation of the $^3\Pi_{0^+u}$ wave function under case c influence by a $^1\Sigma^+_u$ state lying above the $^3\Pi_{0^+u}$.[2]

ROBERT S. MULLIKEN

Ryerson Physical Laboratory,
University of Chicago,
April 14, 1936.

[1] A. P. Acton, R. G. Aickin and N. S. Bayliss, J. Chem. Phys. **4**, 474 (1936).
[2] R. S. Mulliken, Phys. Rev. **46**, 549 (1934).
[3] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 547 1936).

The Crystal Structure of Thallium Trithionate, $Tl_2S_3O_6$

The crystal structure of thallium trithionate has been investigated. Contrary to the statement in literature[1] it has been found not to be isomorphous with that of the corresponding potassium salt.[2, 3] The salt was prepared from equivalent portions of barium trithionate and thallous sulfate; it crystallizes in elongated rectangular tables or flat prisms.

By means of rotation- and oscillation-diagrams the symmetry was found to be monoclinic with the following dimensions of the elementary cell:

$$a=13.20\pm0.05\text{A}, \quad b=7.45\pm0.02\text{A}, \quad c=7.58\pm0.02\text{A}, \quad \beta=91°0.$$

The number of molecules $Tl_2S_3O_6$ in this cell, calculated with the pycnometric density $d=5.08$, was found to be $Z=3.83\leqq4$. The roentgenographic density and molar volume were calculated as $d_{ro}=5.31$, MV=113.0. The b axis, at right angles with the symmetry plane, lies in the direction of the longest dimension of the crystals, the faces of which are formed predominating by 100 and secondary by 101.

The space group was found to be $C_{2h}^6(C2/c)$, the eight thallium atoms occupying the general position $8(f)$: $x\,y\,z$, $\bar{x}\,\bar{y}\,\bar{z}$, $\bar{x}\,y\,\frac{1}{2}-z$, $x\,\bar{y}\,\frac{1}{2}+z$ and the same $+\frac{1}{2}\,\frac{1}{2}\,0$, with the parameter values: $x=0.14\pm0.005$, $y=0.16\pm0.01$ and $z=0.36\pm0.005$.

On account of their low scattering power the positions of sulfur and oxygen atoms could not be determined with accuracy. Of the 12 sulfur atoms four will be occupying the four equivalent position $4(e)$ with the point-symmetry C_2, the other positions having the point-symmetry C_i, resulting in linear S_3 groups. The other sulfur and oxygen atoms will probably be all in general positions. The symmetry of the S_3O_6 group is in this way found to be C_2, the groups situated at right angles with the twofold axis, on which the middle sulfur atom of each group will be lying. This symmetry is in accordance with the results obtained by Zachariasen from the analysis of $K_2S_3O_6$. The molar volume of the thallium trithionate, 113.0, is low in comparison with those of the potassium and rubidium salts 116.3 and 125.2. The molar volumes of thallium salts are generally[4] 2.5 cm³ for one metal atom higher, resp. 1.5 cm³ lower, than those of the corresponding potassium and rubidium salts. These values indicate a rather important difference between the crystal structures of thallium and of potassium trithionate.

Data concerning ammonium trithionate, which is also monoclinic, will be given later.

J. A. A. KETELAAR
J. K. SANDERS

Laboratory of Inorganic Chemistry
of the University, Leyden (Holland),
July 27, 1936.

[1] E. J. Bevan, Chem. News **36**, 203 (1877).
[2] W. H. Zachariasen, J. Chem. Phys. **2**, 109 (1934); Zeits. f. Krist. **A89**, 529 (1934).
[3] The rubidium salt was found to be wholly isomorphous with the potassium salt. The dimensions of the elementary cell are: $a=9.93\pm0.02$A, $b=14.20\pm0.05$A, $c=5.86\pm0.02$A, MV=125.2.
[4] W. Biltz, *Raumchemie der festen Stoffe* (Leipzig, 1934).

A Concentration of the Carbon Isotope

Urey and Greiff[1] pointed out that it should be possible to change the ratio of the isotopes of an element by making use of chemical exchange reactions in conjunction with a counter-current scrubbing apparatus of the type of fractionation columns. In such a method it is necessary to use a two-phase system, gas and liquid. The gas takes the place of the vapor and a solution the place of the liquid in the usual counter-current distillation. Calculations were reported in their paper showing that the equilibrium constants for exchange reactions involving isotopes of the lighter elements, were not exactly unity and in some cases that they differed from unity by as much as nine percent. It was also pointed out that the use of a bicarbonate solution as the liquid phase and carbon dioxide as the gas phase, should be useful for such methods as applied to the carbon isotopes. Though the experiments made to date are not entirely satisfactory, we wish to report them briefly at this time, since difficulties with analytical procedures will delay the completion of our work for some months.

In the initial attempts to make use of the exchange reaction between bicarbonate ion and carbon dioxide, no increased concentrations could be secured. In these experiments a bicarbonate solution was passed through a fractionation column, acid added to the solution at the bottom, and the carbon dioxide passed back through the fractionation column. Since we were not able to calculate the equilibrium constant for this exchange reaction it seemed possible that the equilibrium constant for the reaction was very nearly unity. However, it was called to our attention that the reaction between carbon dioxide and water to give carbonic acid is a slow reaction which is catalyzed by an enzyme, carbonic anhydrase, which can be extracted from red blood cells.

A crude solution of carbonic anhydrase was prepared according to the directions of Meldrum and Roughton,[2] by mixing ox blood cells with 0.4 their volume of ethyl alcohol, 0.6 their volume of water, and then shaken with 0.5 their volume of chloroform. After centrifuging, the supernatant enzyme solution was used directly without further purification.

When the enzyme solution was added to potassium bicarbonate solution, and then used in the way indicated above, an immediate increase of the concentration of C^{13} in the liquid phase was secured. The difference in concentration between this carbon and normal carbon was only a few percent and hence the detection lay just within the limits of the analytical method.

During the past year we have constructed a very efficient fractionation column as described in another letter in this issue. Potassium bicarbonate solution containing about 25 percent by weight of the salt, was pumped into the top of the column by a proportioning pump. At the bottom of the column a cascade of three flasks in series was used to liberate the carbon dioxide. Sulphuric acid was run into the first flask attached directly to the bottom of the column at a constant rate sufficient to neutralize the potassium bicarbonate solution. The flask was heated so that a vigorous evolution of carbon dioxide occurred. The overflow from this flask passed into a second flask which was heated and the water condensed and run into the first flask. The overflow from the second flask was passed through a third flask arranged in the same way. The overflow from the third flask contained no carbon dioxide that we could detect.

The potassium bicarbonate solution in the first run was passed in at the rate of 50 cc per minute and in a second run at the rate of 100 cc per minute. After 45 hours of steady operation the carbon from the first of these runs analyzed 1.36 percent C^{13} instead of 1.06 percent, which we take as a natural abundance. In the second run at the end of 12 hours operation, the carbon analyzed 1.21 percent. For some reason which we do not understand at present, the contents of the column amounting to approximately 2000 grams of potassium bicarbonate, showed carbon of the same composition as the sample removed from the bottom of the column. This indicates that only a small fraction of the 35-foot fractionation column produced any change in the isotope composition.

The column contained approximately 240 grams of carbon as carbon dioxide and bicarbonate ion. The 0.3 percent increase in concentration means, therefore, that in the first experiment 0.78 gram of C^{13} was transferred from normal carbon to a higher concentration in the course of 45 hours and in the second experiment approximately 0.39 gram was transferred in 12 hours. From this it is possible to estimate the simple process fractionation factor for this method since the net amount transferred to the bottom of the column must be qual to the difference in concentration of carbon in the carbon dioxide escaping and the carbon in the bicarbonate solution entering the column multiplied by the total mass of carbon used in these experiments. Calculating in this way we find that the simple process fractionation factor in the first run is approximately 1.013, and in the second run approximately 1.014. Since it cannot be assumed that equilibrium conditions were maintained at the top of the column throughout the run, the simple process fractionation factor may be larger than these numbers. It is interesting to note that this fractionation factor is approximately the same as that calculated by Urey and Greiff for the carbonate ion-carbon dioxide exchange reaction. Further work is in progress on this exchange reaction.

Though the increased concentration secured in these experiments is small, the fact that only a small fraction of the column must have been operating gives us reason to believe that considerably greater concentrations can be secured eventually. Moreover, the transport of heavy material in these experiments is very much as compared with other methods which have been used. The amounts of C^{13} transported from the low concentration material to the higher concentration are approximately one thousand times as great as those secured by the Hertz diffusion method in the same lengths of time.

We are indebted to Dr. W. W. Lozier for analyses of carbon samples using a mass spectrometer built for us by a grant from the Carnegie Institution of Washington, and also to Dr. Sampson of Princeton University for a certain

number of analyses in connection with these experiments. The apparatus used by him was built from funds furnished by the American Philosophical Society. We should also say that we are indebted to Dr. Walker Bleakney of Princeton University for many courtesies in connection with the analysis of our samples.

HAROLD C. UREY
A. H. W. ATEN, JR.
ALBERT S. KESTON

Columbia University,
New York, N. Y.,
August 7, 1936.

[1] Urey and Greiff, J. Am. Chem. Soc. **57**, 321 (1935).
[2] Meldrum and Roughton, J. Physiol. **80**, 113 (1933).

The Concentration of the Oxygen Isotopes

As Lewis and Cornish[1] showed, there is a difference in vapor pressures of the O^{16} and O^{18} varieties of water. Experiments by Wahl and Urey show that this ratio of vapor pressures amounts to approximately 1.003 at the boiling point of water, and approximately 1.008 at 45° centigrade. This small difference in vapor pressure may be used for the concentration of the O^{16} isotope if sufficiently efficient fractionation columns can be constructed. Simple calculations show that such a column must have approximately 500 theoretical plates in order to produce increased concentrations of the isotopes sufficient to make possible an eventually complete separation of O^{18}. At the time this work was begun no such columns had been devised. One of us (G. B. P.)[2] suggested the use of alternate rotating and stationary cones in order to secure a very long path without making the column prohibitively long. The apparatus as at present constructed is 35 feet long and contains 619 rotating cones and 619 stationary cones. The rotating cones are attached to a shaft placed in the center of a 6″ tube. The stationary cones are attached to the tube. The distance between two stationary cones is $\frac{5}{8}$ of an inch and the rotating cones are placed as nearly as possible midway between stationary cones. In this way water drops from a fixed cone to a rotating cone, is carried by centrifugal force up and off to the walls of the tube and then drains under gravity to the center and drops to the next rotating cone. A complete description of this apparatus will be published later.

First experiments were made on a column containing 14 stationary and 14 rotating cones and later with a 5-foot section containing 90 cones of each variety and finally experiments have been made with a 35-foot column as described above. The initial experiment indicated that a theoretical plate is secured for approximately each pair of cones. In the case of the 5-foot section the results were not quite so good, approximately 75 theoretical plates being secured as shown by the separation of the oxygen isotopes of water using the ratio of vapor pressures as determined by Wahl and Urey. Using the 35-foot column a change in the ratios of the oxygen isotopes by a factor of 2 was secured. In these experiments a large container of water was used at the bottom and total reflux was used at the top. In this way water containing less O^{18} than the natural abundance was produced at the top. It required approximately four days for a stationary state to be established, after which no change in the concentration of the isotopes occurred. This is very much less than was expected on the basis of our experiments with shorter columns. The water in the boiler at the bottom was heated by steam and no careful attempts were made to control the rate of boiling precisely. Approximately 100 cc of water were boiled through the column per unit time and considerable fluctuations were noted in the back pressure on the column.

In the most recent experiments with the 35-foot column a flash boiler has been placed at the bottom of the column capable of boiling approximately 50 cc of water per minute. Water has been pumped into the top of the column with a proportioning pump and the water vapor issuing from the top of the column has been condensed and run to the sewer. The run was made under 20 centimeters pressure at the top of the column and water was introduced at the rate of approximately 45 cc per minute. The apparatus operated steadily, day and night, for eight days. At the end of this time the oxygen isotope concentration at the bottom of the column had been increased by the factor of 3 from the natural abundance and the deuterium content by a factor of approximately 40. These figures would indicate that the column operated at approximately 230 theoretical plates, a considerably smaller number than expected on the basis of preliminary experiments. Considerable difficulty was encountered in keeping the proportioning pump operating steadily because of rust collecting in the valves of the pump. It stopped operation completely on several occasions for periods of time that were unknown since the column was not attended except occasionally during this time. Also, an accident occurred in adjusting the pump which caused it to introduce approximately 150 cc of water per minute for a period of perhaps one hour. Such irregularities are certain to cause a decreased efficiency of the column. Considering these difficulties the increased concentration appears to be as good as could be expected. A steady state was not reached as shown by analyses on the last two days.

Analyses were made by passing water samples mixed with hydrogen over platinized asbestos at a temperature of approximately 350° centigrade to promote the exchange between water and hydrogen. In this way it was possible to bring the concentration of deuterium to very near normal concentration. The water samples were then diluted with distilled water and density difference determined by the pressure float method of Gilfillan.[3]

We are indebted to the Carnegie Institution of Washington for a grant for the material required for building the column and its accessory apparatus.

HAROLD C. UREY
G. B. PEGRAM
JOHN R. HUFFMAN

Columbia University,
New York, N. Y.,
August 7, 1936.

[1] Lewis and Cornish, J. Am. Chem. Soc. **55**, 2616 (1933).
[2] G. B. Pegram, Phys. Rev. **49**, 883 (1936).
[3] Gilfillan, J. Am. Chem. Soc. **56**, 406 (1934).

Electrical Properties of Films of ω-Bromo-Hexadecanoic Acid

It has been shown that the potential difference at an air solution interface is shifted to more negative values if halogenated aliphatic compounds are introduced in the solution.[1] This can be explained if we assume that the halogen atoms are orientated outwards by surface forces. No data concerning insoluble compounds which could give analogous effects have been available until now. Through the kindness of Dr. M. Stoll (Geneva, Research Laboratory of Chuit-Naef and Co.) we were able to investigate the behavior of films of $Br-(CH_2)_{15}-COOH$. The relation between surface pressure, potential difference and area per molecule for $Br-(CH_2)_{15}-COOH$ on 0.01 N KCl+10^{-4} N HCl is given in Fig. 1. As shown by Fig. 1, remarkably high negative potential differences are observed. Under certain conditions, still higher values up to −0.87 v have been found. It must be kept in mind that the corresponding nonsubstituted compound, i.e., palmitic acid, gives a positive potential difference with a limiting value of about 0.39 v. The difference 1.26 v is to be considered as due to the orientation of C−Br linkages. The calculated effect should be 2.9 v assuming the area per molecule to be 20 sq. A, the dipole moment of the C−Br linkage $\mu=1.9\times10^{-18}$ and the angle between the C−Br linkage and the water surface 109° 28′/2. The main reason for the discrepancy between the calculated and the observed values of the potential difference lies certainly in the mutual polarization of the C−Br linkages; the interaction with water molecules can be neglected in this case.

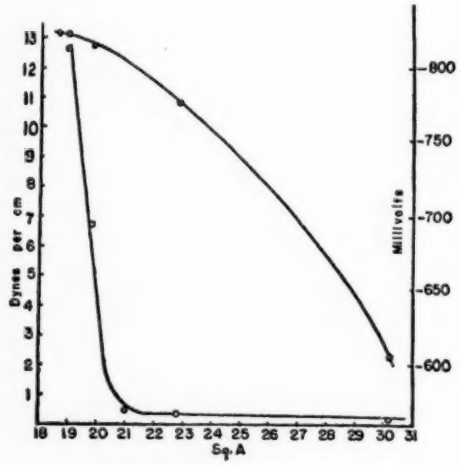

FIG. 1.

A remarkable change in the properties of the film occurs if the acidity of the underlying solution is increased above 5×10^{-4} N. The surface pressure decreases strongly, and the negative effect is changed into a positive one with a limiting value of about 0.07 v on 0.01 N KCl+10^{-3} N HCl. The observed phenomenon is probably due to a change of the structure of the film and not to a hydrolysis of $Br-(CH_2)_{15}-COOH$ into $OH-(CH_2)_{15}-COOH$. The latter compound gives on 0.01 N KCl+10^{-3} N HCl a limiting value of the potential difference equal to 0.22 v. The investigation of the properties of these films is being continued and a detailed account will be published in the *Acta physicochimica U.R.S.S.* We are very much indebted to Dr. M. Stoll who generously supplied one of us with samples of some ω-substituted long-chain compounds, without which this investigation would have been impossible.

M. GEROVICH
A. FRUMKIN

Electrochemical Laboratory,
University of Moscow,
August 13, 1936.

[1] D. A. Frumkin, Zeits. f. physik. Chemie 111, 190 (1924); S. Zofa, A. Frumkin and P. Tshugrenoff, Acta physicochimica U.R.S.S. 1, 880 (1936).

Liquid Propane. Electrical Conductance and Dielectric Constant

We have constructed conductivity cells of glass with platinum electrodes[1] which were used in a study on liquid hydrogen chloride. The same apparatus served to measure the specific conductance of liquefied propane.

The value found was less than 5×10^{-13} reciprocal ohm at 1 kilocycle in the temperature range: −90° to +15°C. From the balancing condensers we were able to determine the dielectric constant (ϵ) of liquid propane as follows:

$$\epsilon_t=\epsilon_0(1+\alpha t);$$
$$\epsilon_0=1.61; \quad \alpha=-0.00124; \quad t=°\text{C}.$$

From the density of liquid propane[2] and the dielectric constant we calculated the molecular polarization to be 14.3 cc independent of the temperature.

GEO. GLOCKLER
R. E. PECK

School of Chemistry,
University of Minnesota,
August 17, 1936.

[1] G. Glockler and R. E. Peck, J. Chem. Phys. in press.
[2] *International Critical Tables*, III, page 228.